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(54) Title: FUNGICIDAL 1,3,4-OXADIAZINES AND 1,3,4-THIADIAZINES			
<div style="text-align: center;"> <p>(I)</p> </div>			
(57) Abstract			
<p>Fungicidal 1,3,4-oxadiazines and 1,3,4-thiadiazines of general formula (I) are disclosed, wherein G<sup>1</sup> is -CR<sup>1</sup>R<sup>7</sup>-, -(CHR<sup>1</sup>CHR<sup>2</sup>)-, -(CHR<sup>1</sup>CHR<sup>2</sup>CHR<sup>3</sup>)-, or -(CHR<sup>1</sup>CHR<sup>2</sup>CHR<sup>3</sup>CHR<sup>4</sup>)-; G<sup>2</sup> is -O-, -S-, -S(O)-, -S(O)<sub>2</sub>-, or -NR<sup>27</sup>-; G<sup>3</sup> is -CR<sup>4</sup>R<sup>8</sup>-, -(CHR<sup>5</sup>CHR<sup>6</sup>)-, or -(CHR<sup>3</sup>CHR<sup>5</sup>CHR<sup>6</sup>)- or a direct bond; X is N or CR<sup>13</sup>; Y is N or CR<sup>13</sup>; and E, R<sup>9</sup>, and R<sup>10</sup> are various groups.</p>			

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TITLE

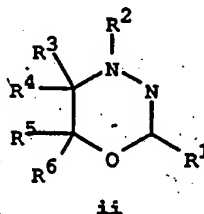
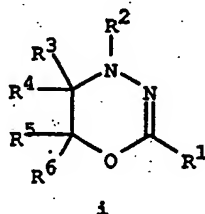
## FUNGICIDAL 1,3,4-OXADIAZINES AND 1,3,4-THIADIAZINES

This invention relates to heterocyclic thiadiazines  
5 and related heterocycles useful as agricultural  
fungicides and compositions containing them.

BACKGROUND OF THE INVENTION

U.S.S.R. patent 461,929 generically discloses  
oxadiazines of Formula i and ii

10



wherein:

15  $R^1$ ,  $R^3$ ,  $R^4$ ,  $R^5$ , and  $R^6$  are hydrogen, alkyls,  
carboxyalkyls, aminoalkyls, phenyl, substituted  
phenyls, pyridyls, quinolyls, furyls, or  
thienyls, and

$R^2$  is alkyl, substituted alkyl, phenyl, substituted  
phenyl, or heteroaryl.

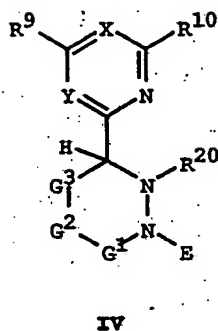
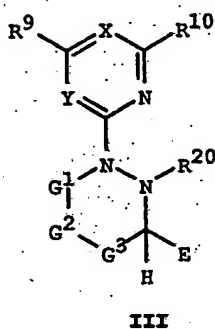
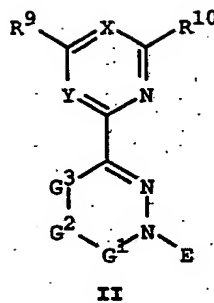
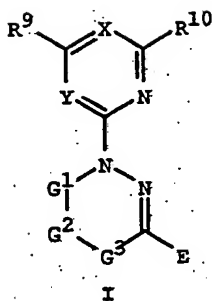
20 U.S.S.R. 461,929 does not specifically name any of  
the compounds of the instant invention, nor is any  
utility for the compounds disclosed, in this patent.

SUMMARY OF THE INVENTION

This invention pertains to compounds of Formulae I,  
25 II, III and IV including all geometric and stereo-  
isomers, agriculturally-suitable salts thereof,  
agriculturally-suitable metal complexes thereof,  
compositions containing them and their use as  
fungicides.

30

2



5 wherein:

-G<sup>1</sup>-G<sup>2</sup>-G<sup>3</sup>- taken together with the attached atoms  
form a 5-8 membered ring, wherein

-G<sup>1</sup>- is -CR<sup>1</sup>R<sup>7</sup>-; -(CHR<sup>1</sup>CHR<sup>2</sup>)-; -(CHR<sup>1</sup>CHR<sup>2</sup>CHR<sup>3</sup>)-; or  
-(CHR<sup>1</sup>CHR<sup>2</sup>CHR<sup>3</sup>CHR<sup>4</sup>)-;

10 -G<sup>2</sup>- is -O-; -S-; -S(O)-; -S(O)<sub>2</sub>- or -NR<sup>27</sup>-;

-G<sup>3</sup>- is -CR<sup>4</sup>R<sup>8</sup>-; -(CHR<sup>5</sup>CHR<sup>6</sup>)-; -(CHR<sup>3</sup>CHR<sup>5</sup>CHR<sup>6</sup>)- or a  
direct bond;

For example, -G<sup>1</sup>-G<sup>2</sup>-G<sup>3</sup>- can be

-CHR<sup>1</sup>CHR<sup>2</sup>-S-CR<sup>4</sup>R<sup>8</sup>-, wherein -G<sup>1</sup>- is

15 -(CHR<sup>1</sup>CHR<sup>2</sup>)-, -G<sup>2</sup>- is -S-, and -G<sup>3</sup>- is -CR<sup>4</sup>R<sup>8</sup>-.

The directionality of the -G<sup>1</sup>-G<sup>2</sup>-G<sup>3</sup>- linkage is  
defined as -G<sup>1</sup>-G<sup>2</sup>-G<sup>3</sup>- in compounds of Formulae  
I and III and -G<sup>3</sup>-G<sup>2</sup>-G<sup>1</sup>- in compounds of

Formulae II and IV. Therefore, for example,

20 when -G<sup>1</sup>- is -(CHR<sup>1</sup>CHR<sup>2</sup>)- in a compound of  
Formula I or III, then the carbon of the CHR<sup>2</sup>  
unit of -G<sup>1</sup>- is bonded to -G<sup>2</sup>-. In a compound



of Formula II or IV, when  $-G^1-$  is  $-(CHR^1CHR^2)$ ,  
the carbon of the  $CHR^1$  unit is bonded to  $-G^2-$ .

X is N or  $CR^{13}$ ;

Y is N or  $CR^{14}$ ;

5 E is H;  $C_1-C_6$  alkyl;  $C_3-C_7$  cycloalkyl optionally  
substituted with 1-2 methyl;  $C_1-C_6$  haloalkyl;  
 $C_1-C_6$  alkylthio;  $C_1-C_6$  alkoxy;  $C_1-C_6$  haloalkoxy;  
or phenyl, phenoxy, phenylthio, phenylamino,  
phenylmethyl, indanyl, tetrahydronaphthalenyl,  
10 1-naphthalenyl, 2-naphthalenyl, thienyl,  
furanyl or pyridyl each optionally substituted  
with  $R^{11}$ ,  $R^{12}$  and  $R^{28}$ ;

$R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are each  
independently H;  $C_1-C_4$  alkyl;  $C_1-C_4$  haloalkyl,  
15 halogen,  $CO_2CH_3$ ,  $CO_2CH_2CH_3$ , cyano or phenyl  
optionally substituted with  $R^{25}$ ;

provided that

(i) when  $-G^1- = -CR^1R^7-$  and  $-G^3- = -CR^4R^8-$ ,  
then at least one of  $R^1$ ,  $R^4$ ,  $R^7$  and  $R^8$  is  
20 hydrogen; in other words the maximum  
number of carbon atoms in  $-G^1-G^2-G^3-$  with  
geminal disubstitution is one;

(ii) the maximum number of optionally  
substituted phenyl substituents on  
25  $-G^1-G^2-G^3-$  is one;

(iii)  $-G^3-$  is other than a direct bond in  
compounds of Formulae III and IV; and

(iv)  $-G^2-G^3-$  is other than  $-NR^{27}-$  in compounds  
of Formulae I and II;

30  $R^9$ ,  $R^{10}$  and  $R^{13}$  are each independently H; halogen;  
cyano; hydroxy;  $C_1-C_6$  alkyl;  $C_1-C_4$  haloalkyl;  
 $C_1-C_4$  alkylthio;  $C_1-C_4$  alkylsulfinyl;  $C_1-C_4$   
alkylsulfonyl;  $C_3-C_6$  cycloalkyl optionally  
substituted with 1-2 methyl groups;  $C_1-C_4$   
35 alkoxy;  $C_1-C_4$  haloalkoxy;  $C_2-C_4$  alkoxyalkyl;  
 $C_2-C_4$  alkenyl;  $C_2-C_4$  haloalkenyl;  $C_2-C_4$

- alkenyloxy; C<sub>2</sub>-C<sub>4</sub> alkynyl; C<sub>2</sub>-C<sub>4</sub> alkynyloxy;  
NR<sup>29</sup>R<sup>30</sup>; or phenyl or phenoxy optionally  
substituted with R<sup>31</sup>; or  
R<sup>9</sup> and R<sup>13</sup>, or R<sup>10</sup> and R<sup>13</sup>, or R<sup>9</sup> and R<sup>14</sup> can be  
5 taken together to form -(CH<sub>2</sub>)<sub>3</sub>-, -(CH<sub>2</sub>)<sub>4</sub>- or a  
fused benzene ring optionally substituted with  
R<sup>31</sup>;  
R<sup>11</sup>, R<sup>12</sup>, R<sup>21</sup>, R<sup>24</sup>, R<sup>26</sup> and R<sup>31</sup> are each  
independently halogen; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub>  
10 haloalkyl; C<sub>1</sub>-C<sub>4</sub> alkoxy; or C<sub>1</sub>-C<sub>4</sub> haloalkoxy;  
R<sup>14</sup> is H; halogen; C<sub>1</sub>-C<sub>2</sub> alkyl; or C<sub>1</sub>-C<sub>2</sub> alkoxy;  
R<sup>15</sup>, R<sup>16</sup>, R<sup>17</sup>, R<sup>18</sup>, R<sup>29</sup> and R<sup>30</sup> are each  
independently H or C<sub>1</sub>-C<sub>2</sub> alkyl; or  
R<sup>15</sup> and R<sup>16</sup>, or R<sup>17</sup> and R<sup>18</sup>, or R<sup>29</sup> and R<sup>30</sup> can be  
15 taken together along with the nitrogen atom to  
which they are attached to form a  
4-morpholinyl, pyrrolidinyl or piperidinyl  
ring;  
R<sup>20</sup> and R<sup>27</sup> are each independently H; C<sub>1</sub>-C<sub>4</sub> alkyl;  
20 C<sub>1</sub>-C<sub>4</sub> haloalkyl; C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl; phenyl-  
carbonyl optionally substituted with R<sup>21</sup>; C<sub>3</sub>-C<sub>4</sub>  
alkenyl; C<sub>3</sub>-C<sub>4</sub> alkynyl; phenylmethyl optionally  
substituted with R<sup>21</sup> on the phenyl ring; C<sub>1</sub>-C<sub>4</sub>  
alkylsulfinyl; C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl; phenyl-  
25 sulfinyl, phenylsulfonyl or phenoxycarbonyl  
each optionally substituted with R<sup>21</sup>; C<sub>2</sub>-C<sub>4</sub>  
alkoxycarbonyl; C(=O)NR<sup>22</sup>R<sup>23</sup>; C(=S)NHR<sup>23</sup>;  
P(=S)(C<sub>1</sub>-C<sub>4</sub> alkoxy)<sub>2</sub>; P(=O)(C<sub>1</sub>-C<sub>4</sub> alkoxy)<sub>2</sub>; or  
S(=O)<sub>2</sub>NR<sup>22</sup>R<sup>23</sup>;  
30 R<sup>22</sup> is H or C<sub>1</sub>-C<sub>3</sub> alkyl;  
R<sup>23</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl; or phenyl optionally  
substituted with R<sup>24</sup>; or  
R<sup>22</sup> and R<sup>23</sup> can be taken together along with the  
nitrogen atom to which they are attached to  
35 form a 4-morpholinyl, pyrrolidinyl, piperidinyl  
or imidazolyl ring;

R<sup>25</sup> is 1-2 halogen; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy; nitro; cyano or C<sub>1</sub>-C<sub>4</sub> alkylthio;

R<sup>28</sup> is halogen; cyano; nitro; hydroxy;

5 hydroxycarbonyl; C<sub>1</sub>-C<sub>6</sub> alkyl; C<sub>3</sub>-C<sub>6</sub> cycloalkyl; C<sub>1</sub>-C<sub>6</sub> haloalkyl; C<sub>1</sub>-C<sub>4</sub> alkylthio; C<sub>1</sub>-C<sub>4</sub> alkylsulfinyl; C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl; (C<sub>1</sub>-C<sub>4</sub> alkyl)3-silyl; C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl; C<sub>2</sub>-C<sub>4</sub> alkenyl; C<sub>3</sub>-C<sub>4</sub> alkenyloxy; C<sub>2</sub>-C<sub>4</sub> alkynyl; C<sub>3</sub>-C<sub>4</sub> alkynyloxy;  
10 C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy; C<sub>2</sub>-C<sub>4</sub> alkoxy-alkyl; C<sub>2</sub>-C<sub>5</sub> alkoxy-carbonyl; C<sub>2</sub>-C<sub>4</sub> alkoxy-alkoxy; NR<sup>15</sup>R<sup>16</sup>; C(=O)NR<sup>17</sup>R<sup>18</sup>; or phenyl, phenoxy or phenylthio each optionally substituted with R<sup>26</sup>;

15 provided that

when E is, C<sub>1</sub>-C<sub>6</sub> alkylthio, C<sub>1</sub>-C<sub>6</sub> alkoxy, C<sub>1</sub>-C<sub>6</sub> haloalkoxy, phenoxy, phenylthio or phenylamino, then E may only substitute compounds of Formula I.

20 In the above recitations, the term "alkyl", used either alone or in compound words such as "alkylthio" or "haloalkyl" denotes straight-chain or branched alkyl; e.g., methyl, ethyl, *n*-propyl, *i*-propyl, or the different butyl, pentyl or hexyl isomers.

25 "Alkenyl" denotes straight-chain or branched alkenes; e.g., 1-propenyl, 2-propenyl, 3-propenyl and the different butenyl, pentenyl and hexenyl isomers. "Alkenyl" also denotes polyenes such as 1,3-hexadiene and 2,4,6-heptatriene.

30 "Alkenyloxy" denotes straight-chain or branched alkenyloxy moieties. Examples of alkenyloxy include H<sub>2</sub>C=CHCH<sub>2</sub>O, (CH<sub>3</sub>)<sub>2</sub>C=CHCH<sub>2</sub>O, (CH<sub>3</sub>)CH=CHCH<sub>2</sub>O, (CH<sub>3</sub>)CH=C(CH<sub>3</sub>)CH<sub>2</sub>O and CH<sub>2</sub>=CHCH<sub>2</sub>CH<sub>2</sub>O.

35 "Alkynyl" denotes straight-chain or branched alkynes; e.g., ethynyl, 1-propynyl, 3-propynyl and the different butynyl, pentynyl and hexynyl isomers.

"Alkynyl" can also denote moieties comprised of multiple triple bonds; e.g., 2,7-octadiyne and 2,5,8-decatriyne.

5 "Alkynyloxy" denotes straight-chain or branched alkynyloxy moieties. Examples include  $\text{HC}\equiv\text{CCH}_2\text{O}$ ,  $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{O}$  and  $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_2\text{O}$ .

10 "Alkylthio" denotes branched or straight-chain alkylthio moieties; e.g. methylthio, ethylthio, and the different propylthio, butylthio, pentylthio and hexylthio isomers.

Examples of "alkylsulfonyl" include  $\text{CH}_3\text{SO}_2$ ,  $\text{CH}_3\text{CH}_2\text{SO}_2$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{SO}_2$ ,  $(\text{CH}_3)_2\text{CHSO}_2$  and the different butylsulfonyl, pentylsulfonyl and hexylsulfonyl isomers.

15 "Alkylsulfinyl" denotes both enantiomers of an alkylsulfinyl group. For example,  $\text{CH}_3\text{SO}$ ,  $\text{CH}_3\text{CH}_2\text{SO}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{SO}$ ,  $(\text{CH}_3)_2\text{CHSO}$  and the different butylsulfinyl, pentylsulfinyl and hexylsulfinyl isomers.

20 "Alkoxy" denotes, for example, methoxy, ethoxy, n-propyloxy, isopropyloxy and the different butoxy, pentoxy and hexyloxy isomers.

"Cycloalkyl" denotes, for example, cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl.

The term "halogen", either alone or in compound words such as "haloalkyl", denotes fluorine, chlorine, 25 bromine or iodine. Further, when used in compound words such as "haloalkyl", said alkyl may be partially or fully substituted with halogen atoms which may be the same or different. Examples of "haloalkyl" include

30  $\text{F}_3\text{C}$ ,  $\text{ClCH}_2$ ,  $\text{CF}_3\text{CH}_2$  and  $\text{CF}_3\text{CF}_2$ . Examples of "haloalkenyl" include  $(\text{Cl})_2\text{C}=\text{CHCH}_2$  and  $\text{CF}_3\text{CH}_2\text{CH}=\text{CHCH}_2$ .

Examples of "haloalkynyl" include  $\text{HC}\equiv\text{CCHCl}$ ,  $\text{CF}_3\text{C}\equiv\text{C}$ ,  $\text{CCl}_3\text{C}\equiv\text{C}$  and  $\text{FCH}_2\text{C}\equiv\text{CCH}_2$ . Examples of "haloalkoxy" include  $\text{CF}_3\text{O}$ ,  $\text{CCl}_3\text{CH}_2\text{O}$ ,  $\text{CF}_2\text{HCH}_2\text{CH}_2\text{O}$  and  $\text{CF}_3\text{CH}_2\text{O}$ .

35 The total number of carbon atoms in a substituent group is indicated by the " $\text{C}_i\text{-C}_j$ " prefix where i and j

are numbers from 1 to 8. For example, C<sub>1</sub>-C<sub>3</sub> alkyl-sulfonyl designates methylsulfonyl through propyl-sulfonyl; C<sub>2</sub> alkoxyalkoxy designates CH<sub>3</sub>OCH<sub>2</sub>O; C<sub>3</sub> alkoxyalkoxy designates, for example, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>O or CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>O; and C<sub>4</sub> alkoxyalkoxy designates the various isomers of an alkoxy group substituted with a second alkoxy group containing a total of 4 carbon atoms, examples including CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>O, and CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>O. Examples of "alkoxyalkyl" include CH<sub>3</sub>OCH<sub>2</sub>, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub> and CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>. Examples of "alkoxycarbonyl" include CH<sub>3</sub>OC(=O), CH<sub>3</sub>CH<sub>2</sub>OC(=O), CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OC(=O), (CH<sub>3</sub>)<sub>2</sub>CHOC(=O) and the different butoxy-, pentoxy- or hexyloxycarbonyl isomers.

Preferred for reasons of greatest fungicidal activity and/or ease of synthesis are

1. Compounds of Formula I wherein:

Y is N;

E is phenyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, thienyl, or pyridyl each optionally substituted with R<sup>11</sup>, R<sup>12</sup> and R<sup>28</sup>;

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are each independently H or methyl;

R<sup>11</sup> and R<sup>12</sup> are each independently F, Cl, methyl, trifluoromethyl, methoxy or trifluoromethoxy;

R<sup>13</sup> is H;

R<sup>9</sup> and R<sup>10</sup> are each independently halogen;

C<sub>1</sub>-C<sub>4</sub> alkyl; cyclopropyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; allyl; or C<sub>2</sub>-C<sub>3</sub> alkynyl; or

R<sup>9</sup> and R<sup>13</sup> can be taken together to form a fused benzene ring optionally substituted with R<sup>31</sup>;

R<sup>28</sup> is halogen; cyano; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub>

haloalkyl; allyl; propargyl; C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy; or phenyl or

phenoxy each optionally substituted with  $R^{26}$ ;

$R^{31}$  is halogen;  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  haloalkyl;

5 and agriculturally-suitable metal complexes thereof.

2. Compounds of Formula III wherein:

Y is N

10 E is phenyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, thienyl, or pyridyl each optionally substituted with  $R^{11}$ ,  $R^{12}$  and  $R^{28}$ ;

$R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are each independently H or methyl;

15  $R^9$  and  $R^{10}$  are each independently halogen;  $C_1$ - $C_4$  alkyl; cyclopropyl;  $C_1$ - $C_4$  haloalkyl; allyl; or  $C_2$ - $C_3$  alkynyl; or

$R^9$  and  $R^{13}$  can be taken together to form a fused benzene ring optionally substituted with  $R^{31}$ ;

20  $R^{11}$  and  $R^{12}$  are each independently F, Cl, methyl, trifluoromethyl, methoxy or trifluoromethoxy;

$R^{13}$  is H;

25  $R^{20}$  is H;

$R^{27}$  is H;  $C_1$ - $C_4$  alkyl;  $C_2$ - $C_5$  alkoxy carbonyl;  $C_3$ - $C_4$  alkenyl or  $C_3$ - $C_4$  alkynyl;

30  $R^{28}$  is halogen; cyano;  $C_1$ - $C_4$  alkyl;  $C_1$ - $C_4$  haloalkyl; allyl; propargyl;  $C_1$ - $C_4$  alkoxy;  $C_1$ - $C_4$  haloalkoxy; or phenyl or phenoxy each optionally substituted with  $R^{26}$ ;

$R^{31}$  is halogen;  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  haloalkyl;

35 and agriculturally-suitable metal complexes thereof.

## 3. Compounds of Preferred 1 wherein:

G<sup>2</sup> is O; S or NR<sup>27</sup>;

E is phenyl optionally substituted with R<sup>11</sup>,  
R<sup>12</sup> and R<sup>28</sup>; indanyl or tetrahydro-  
naphthalenyl; and agriculturally-suitable  
metal complexes thereof.

## 4. Compounds of Preferred 3 wherein:

G<sup>2</sup> is O; S; NH or N(C<sub>1</sub>-C<sub>4</sub> alkyl);

E is phenyl optionally substituted with R<sup>11</sup>,  
R<sup>12</sup> and R<sup>28</sup>; and agriculturally-suitable  
metal complexes thereof.

Specifically preferred for greatest fungicidal  
activity and/or ease of synthesis are:

3-(4,6-dimethyl-2-pyrimidinyl)-3,6-dihydro-5-  
phenyl-2H-1,3,4-oxadiazine

3-(4,6-dimethyl-2-pyrimidinyl)-5-(4-ethylphenyl)-  
3,6-dihydro-2H-1,3,4-oxadiazine

2-(2-chlorophenyl)-4-(4,6-dimethyl-2-  
pyrimidinyl)-5,6-dihydro-4H-1,3,4-thiadiazine

4-(4,6-dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-  
5,6-dihydro-4H-1,3,4-thiadiazine

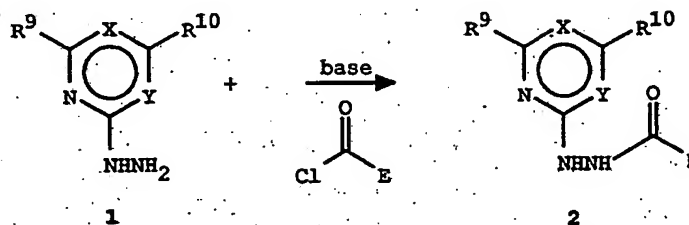
DETAILED DESCRIPTION OF THE INVENTION

Compounds of Formula I wherein E is as described in  
the Summary of the Invention except that E is not  
phenoxy, phenylthio, phenylamino, C<sub>1</sub>-C<sub>6</sub> alkoxy, C<sub>1</sub>-C<sub>6</sub>  
alkylthio and C<sub>1</sub>-C<sub>6</sub> haloalkoxy can be prepared by one  
or more of the methods described in Equations 1-6 and  
13.

Compounds of Formula 2 in Equation 1 can be  
prepared by reacting hydrazine 1 with an acid chloride  
and a base such as pyridine or triethylamine at 0°C in  
a solvent such as dichloromethane, THF, or pyridine  
(Equation 1). The hydrazines 1 are known in the

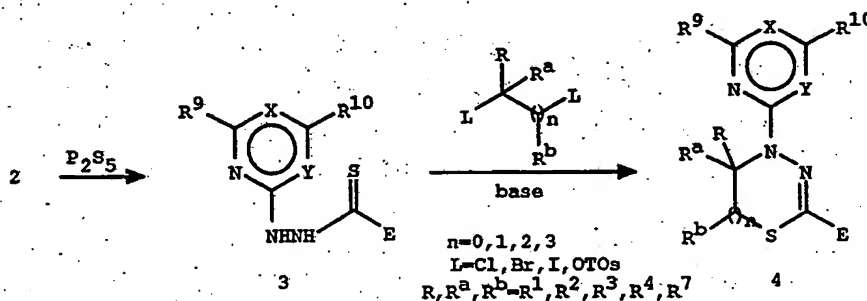
literature (*J. Pest. Sci.*, 1990, 15, 13) and can be prepared by one skilled in the art as taught in EP 293,743-A and by Naito et al. in *Chem. Pharm. Bull.*, 1969, 17, 1467.

5 Equation 1



Compounds of Formula 4 can be prepared by treatment of hydrazides of Formula 2 with  $P_2S_5$  in pyridine at reflux for 1-2 h to form thiohydrazides of Formula 3, followed by reaction with an appropriate alkylating agent, wherein L can be Cl, Br, I or tosylate, in the presence of two equivalents of base, such as triethylamine (Equation 2). In some cases, additional base such as sodium hydride is necessary to induce cyclization. The cyclization reaction is typically performed at 25° to 100°C in an inert aprotic solvent such as THF or acetonitrile.

20 Equation 2



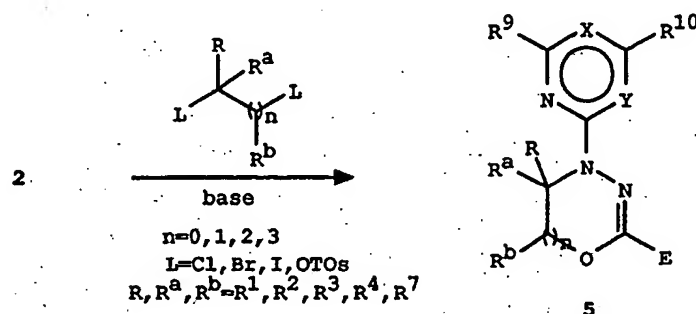
Compounds of Formula 5 can be prepared similarly by treatment of hydrazides of Formula 2 with an alkylating



agent and two equivalents of base using the cyclization procedure previously described for the preparation of compounds of Formula 4 (Equation 3).

Equation 3

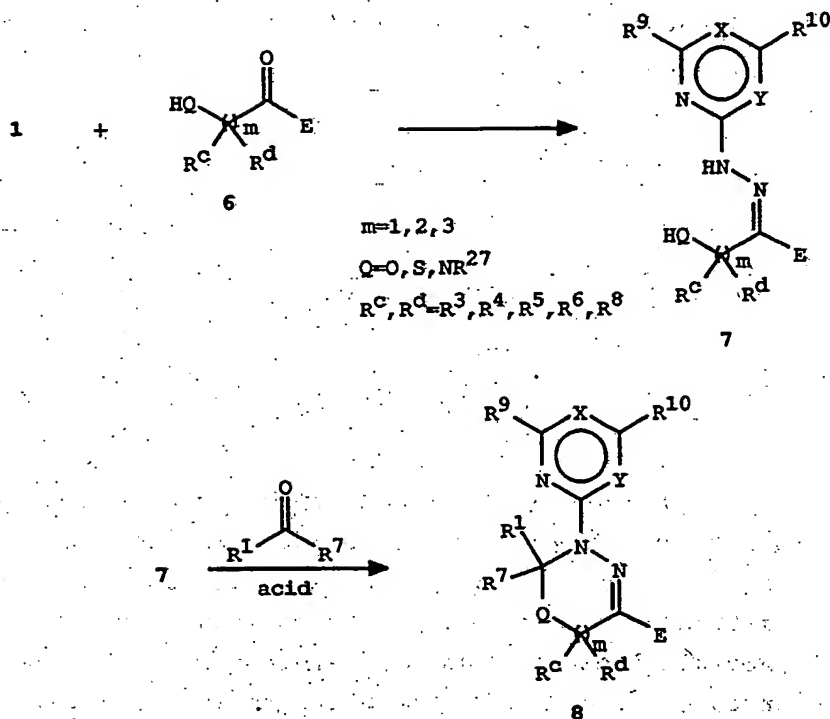
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Compounds of Formula 7 can be prepared by the reaction of hydrazines of Formula 1 with ketones of Formula 6 in a solvent such as acetonitrile, dichloromethane or acetic acid. The desired heterocycles of Formula 8 can be formed by treatment of the resulting product with a ketone or aldehyde in the presence of a catalytic amount of acid such as butanesulfonic acid (Equation 4). This reaction is typically conducted at 25° to 100°C in an anhydrous organic solvent such as THF or acetonitrile for 12 to 24 h.

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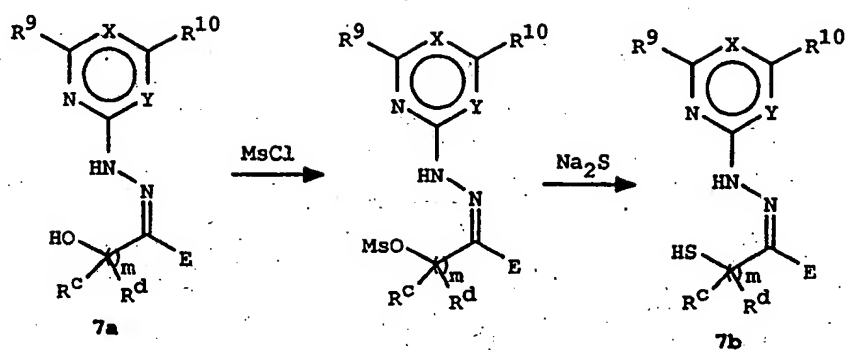
## Equation 4



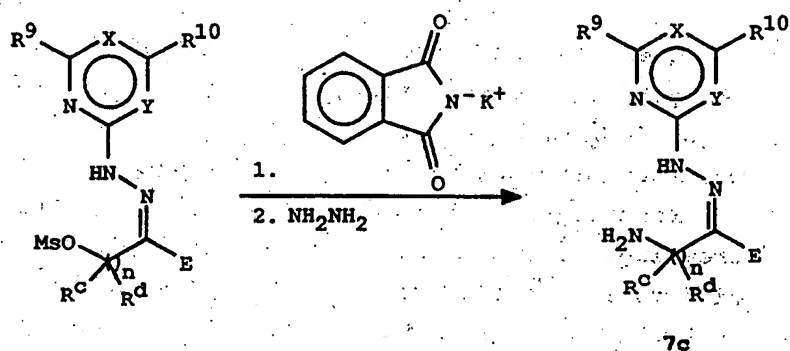
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Compounds of Formula 6 wherein  $m=1$  and  $Q=O$  can be prepared by  $\alpha$ -hydroxylation of a methyl ketone with iodosobenzene as described by Moriarty et al. in *Tetrahedron Lett.*, 1981, 22, 1283.

Thiols of Formula 7b and amines of Formula 7c can be prepared as outlined in Equation 5. Alcohols of Formula 7a ( $Q=O$ ) can be converted to the corresponding mesylate by methods known in the art. The mesylates can be treated with sodium sulfide to form the thiols 7b, or they can be reacted with potassium phthalimide and then hydrazine to form amines of Formula 7c.

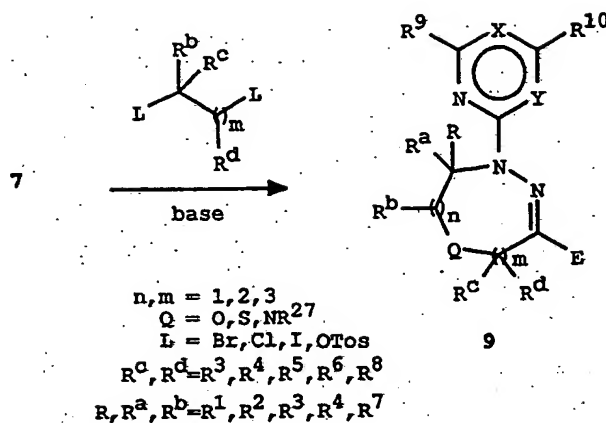
Equation 5

$m=1, 2, 3$   
 $R^C, R^D = R^3, R^4, R^5, R^6, R^8$

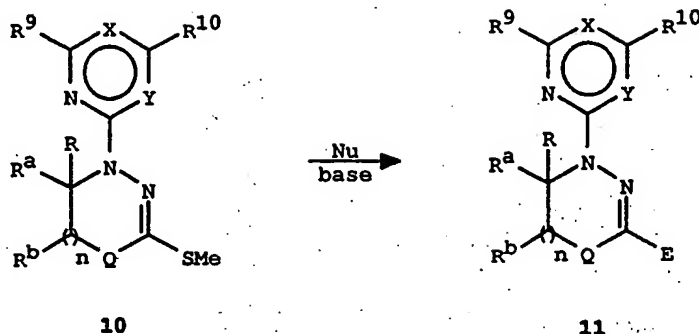


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Formation of heterocycles of Formula 9 can be accomplished by treatment of hydrazones of Formula 7 with the appropriate alkylating agent as previously described for the preparation of heterocycles of Formula 4 (Equation 6).

Equation 6

- 5 Compounds of Formula I wherein E is phenoxy, phenylthio, phenylamino, C<sub>1</sub>-C<sub>6</sub> alkoxy, C<sub>1</sub>-C<sub>6</sub> alkylthio or C<sub>1</sub>-C<sub>6</sub> haloalkoxy can be prepared by one or more of the methods described in Equations 7-13.
- 10 Heterocycles of Formula 11 can be prepared by treating methylthio-substituted compounds of Formula 10 with various nucleophiles in the presence of a base. Suitable nucleophiles can be optionally substituted phenols, thiophenols, or anilines, C<sub>1</sub>-C<sub>6</sub> alkylthiols, C<sub>1</sub>-C<sub>6</sub> alcohols and C<sub>1</sub>-C<sub>6</sub> halo-substituted alcohols
- 15 (Equation 7).

Equation 7

Nu = optionally substituted phenol, thiophenol, or aniline; C<sub>1</sub>-C<sub>6</sub> alkylthiol; C<sub>1</sub>-C<sub>6</sub> alcohol, C<sub>1</sub>-C<sub>6</sub> halo-substituted alcohol

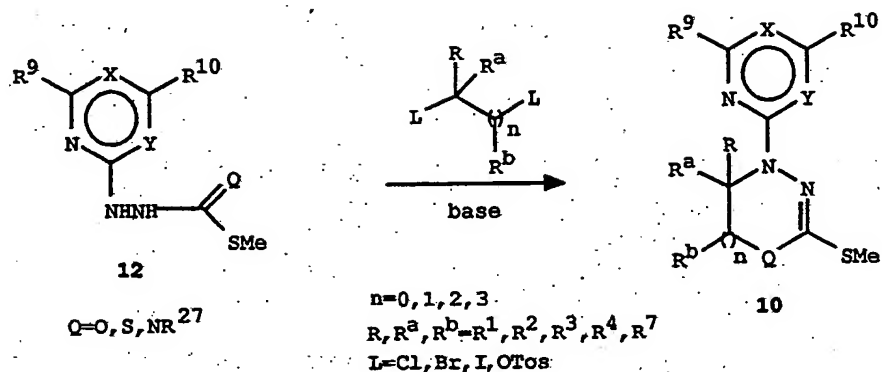
n = 0, 1, 2, 3

Q = O, S, N-R<sup>27</sup>

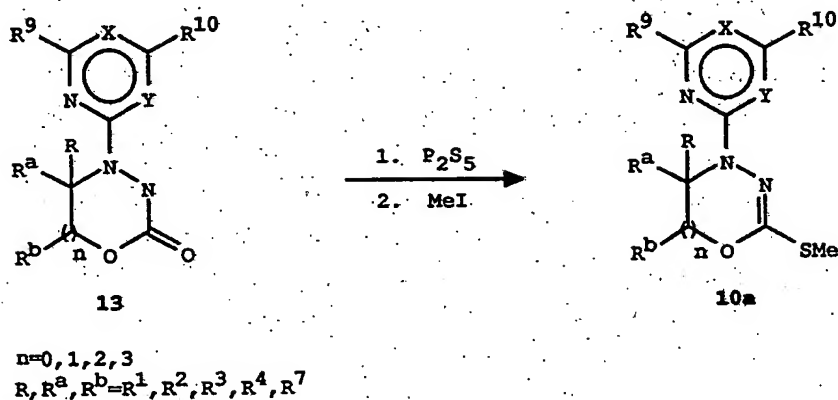
R, R<sup>a</sup>, R<sup>b</sup> = R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>7</sup>

The methythio-substituted heterocycles of Formula 10 can be synthesized by reaction of carbazates of Formula 12 with an alkylating agent in the presence of two equivalents of base, such as triethylamine (Equation 8). This type of cyclization was described previously for the preparation of compounds of Formula 4 (Equation 2). Compounds of Formula 12 are known in the literature and can be prepared by one skilled in the art (e.g., see G. W. Stacy, "Heterocyclic Compounds," R. C. Elderfield, ed., Wiley, NY, 1961, vol. 7, p 835).

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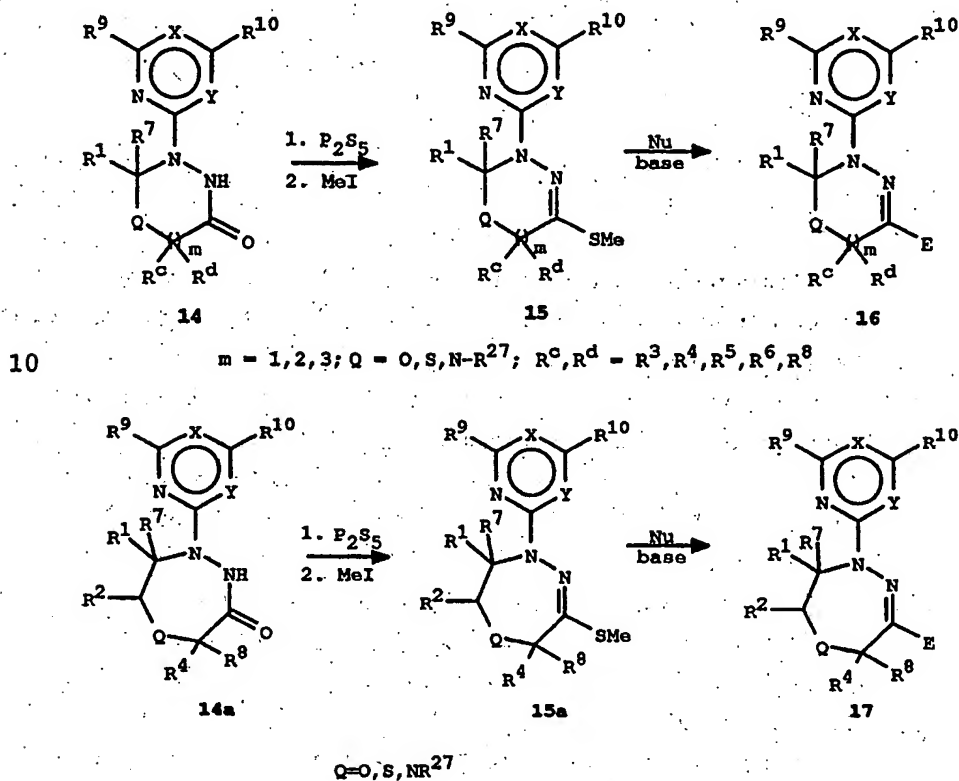
Equation 8

- 5 Alternatively, compounds of Formula 10a can be prepared by sequential treatment of carbazates of Formula 13 with  $P_2S_5$  and iodomethane in pyridine (Equation 9). Carbazates of Formula 13 are known in the literature (e.g., see Dox, *J. Am. Chem. Soc.*, 1926, 48, 1951).

Equation 9

- 15 Methylthio-substituted heterocycles of Formula 15 can be prepared by treating hydrazides of Formula 14 with  $P_2S_5$  in pyridine at reflux and then alkylating the resulting thio derivative with iodomethane in the presence of a base such as triethylamine (Equation 10).

Reaction of compounds of Formula 15 with nucleophiles and base, as previously described for the preparation of compounds of Formula 11 in Equation 7, yields products of Formula 16. The seven-membered ring analogs, compounds of Formula 17, can be prepared from hydrazides of Formula 14a by the same procedure (Equation 10).

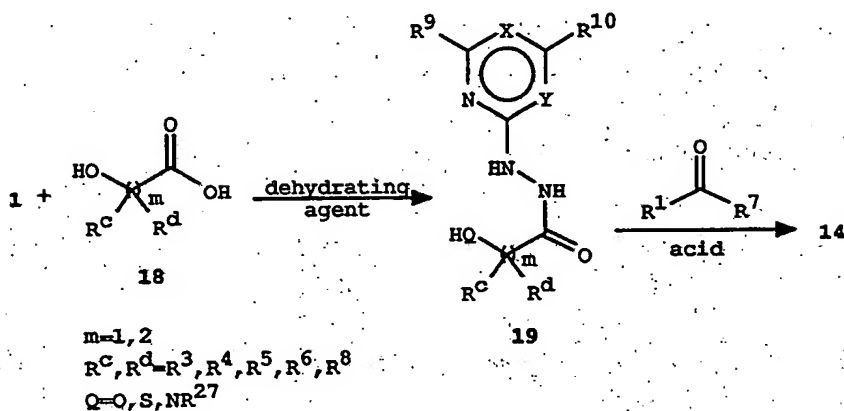
Equation 10

15 Treatment of hydrazides of Formula 19 with an aldehyde or ketone in the presence of a catalytic amount of acid, such as butanesulfonic acid, yields heterocycles of Formula 14 (Equation 11). The cyclization is typically performed at 25° to 100°C in

18

an anhydrous organic solvent such as THF or acetonitrile.

Equation 11

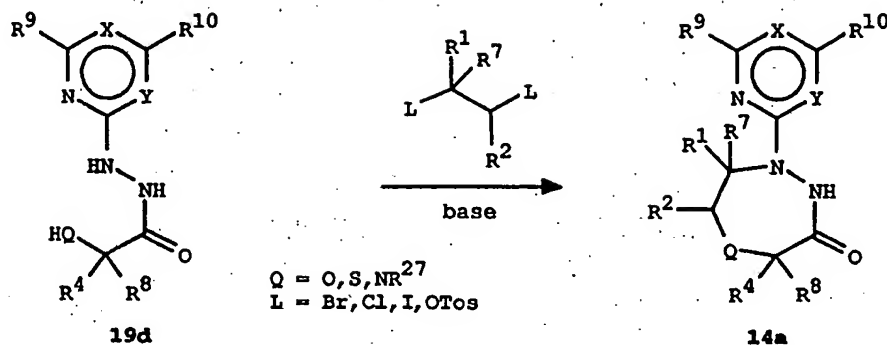


Compounds of Formula 19a (Q=O) can be synthesized by condensing hydrazine 1 with hydroxyacids of Formula 18 in the presence of a dehydrating agent such as dicyclohexylcarbodiimide in an inert aprotic solvent such as THF or dichloromethane. Hydroxyacids of Formula 18 are well-known to one skilled in the art. Thiols of Formula 19b (Q=S) and amines of Formula 19c (Q=NR<sup>27</sup>) can be prepared by forming the mesylate of alcohols of Formula 19a followed by displacement with nucleophiles in a manner similar to that previously described for the preparation of compounds of Formulae 7b and 7c (Equation 5).

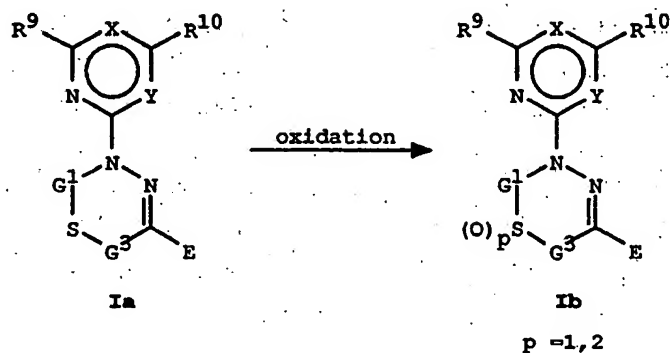
Compounds of 14a can be prepared by treatment of hydrazides of Formula 19d (m=1) with the appropriate alkylating agent, as illustrated in Equation 12, according to procedures described above (see Equations 2 and 3).



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Equation 12

- 5 Compounds of Formula Ib wherein  $G^2$  is  $S(O)$  or  $S(O)_2$  can be prepared from the corresponding thio analogue Ia by well-known methods for oxidation of sulfur (Equation 13). Typical reagents for this type of oxidation include *m*-chloroperoxybenzoic acid, hydrogen peroxide, sodium metaperiodate, and OXONE® (potassium peroxymono-
- 10 sulfates).

Equation 13

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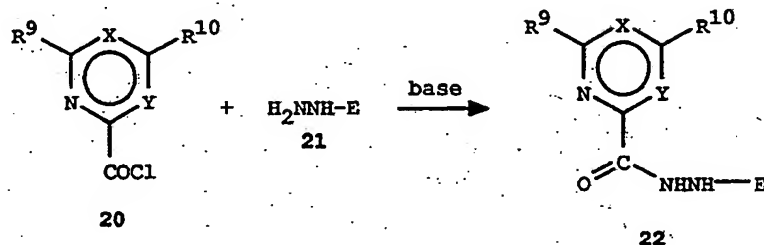
Compounds of Formula II can be prepared by one or more of the following methods described in Equations 14-19.

- Hydrazides of Formula 22 can be synthesized by the
- 20 reaction of hydrazine 21 with an acid chloride of

Formula 20 in the presence of a base such as triethylamine or pyridine (Equation 14). Typical solvents for this reaction are dichloromethane and THF.

Equation 14

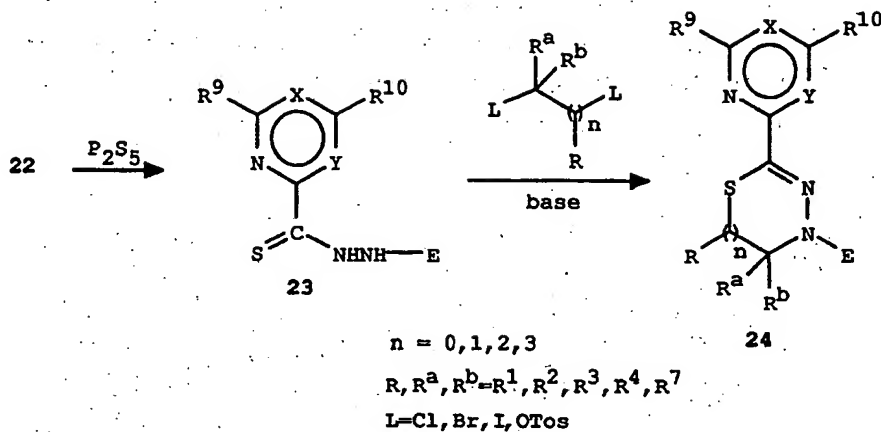
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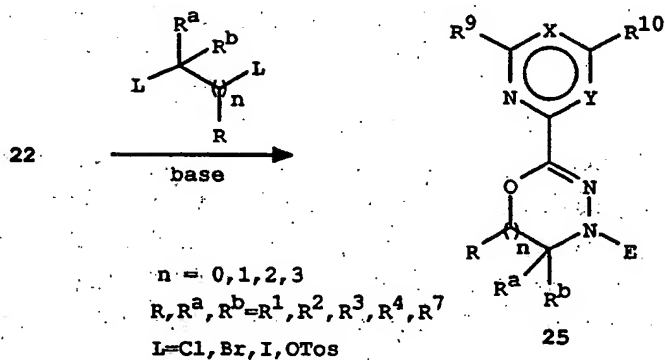
The acid chloride of Formula 20 can be prepared by treatment of the corresponding carboxylic acid with thionyl chloride. Methods for preparing acid chlorides from carboxylic acids are well-known in the literature.

Procedures for preparing pyrimidine carboxylic acids are described by Sakamoto, T., and Yamanaka, H. in *Heterocycles*, 1981, 15, 583.

Heterocycles of Formula 24 can be prepared by treating hydrazides of Formula 22 with  $\text{P}_2\text{S}_5$  in pyridine at reflux to form the thiohydrazides of Formula 23, followed by reaction of 23 with an alkylating agent in the presence of two equivalents of base such as triethylamine (Equation 15). Typically, these reactions are conducted at 25° to 100°C in an inert aprotic solvent such as THF or acetonitrile.

Equation 15

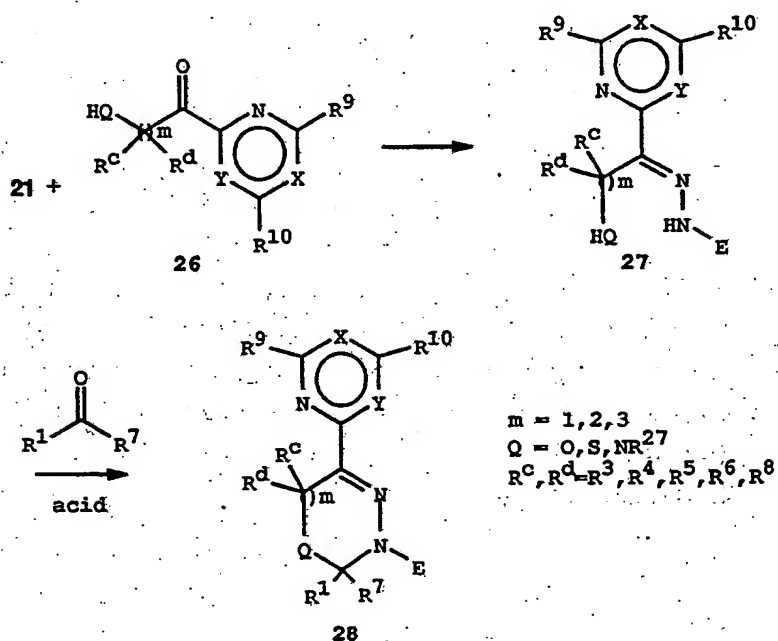
- 5 Compounds of Formula 25 can be prepared similarly by treatment of hydrazides of Formula 22 with an alkylating agent and two equivalents of base according to the previously described cyclization procedure (Equation 16).

10 Equation 16

- 15 Compounds of Formula 28 can be synthesized by the reaction of hydrazines of Formula 21 with ketones of Formula 26 in a solvent such as dichloromethane or acetonitrile to form hydrazones of Formula 27 (Equation 17). The hydrazone can then be treated with a ketone

or aldehyde in the presence of a catalytic amount of acid, such as butanesulfonic acid, to form cycloadducts of Formula 28. This reaction is typically carried out at 25° to 100°C in an anhydrous organic solvent such as THF or acetonitrile.

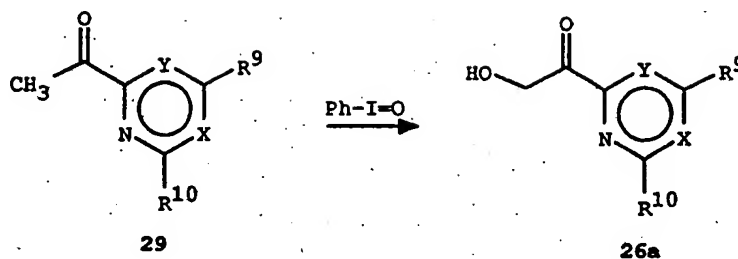
Equation 17



- 10 Hydroxyketones of Formula 26a ( $Q=O, m=1$ ) can be prepared by  $\alpha$ -hydroxylation of the corresponding methyl ketone 29 with iodosobenzene as described by Moriarty et al. in *Tetrahedron Lett.*, 1981, 22, 1283, and illustrated in Equation 18. Methods to prepare
- 15 heteroaryl ketones of Formula 29 are well-known in the art. The corresponding thiols of Formula 26b ( $Q=S$ ) and amines of Formula 26c ( $Q=NR^{27}$ ) can be prepared by methods previously described for thiols and amines of Formulae 7b and 7c, respectively (Equation 5).

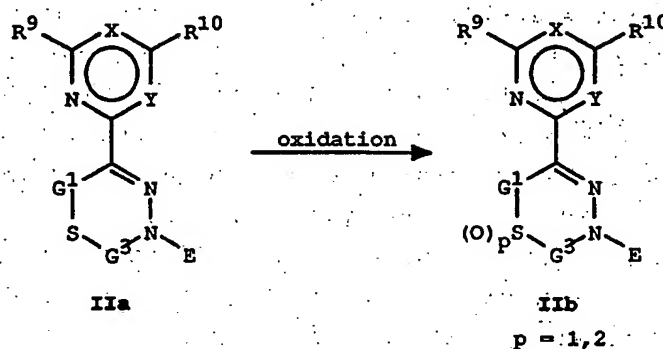
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Equation 18

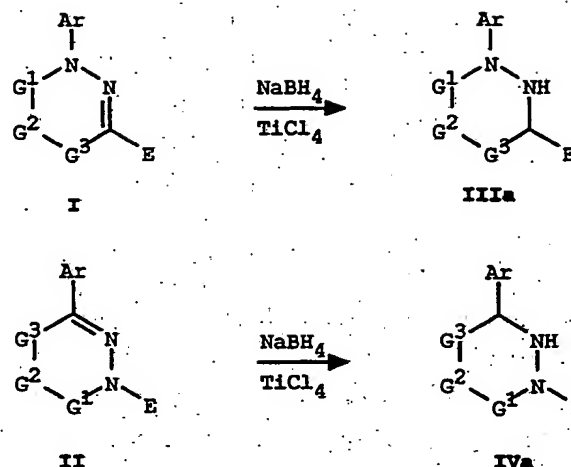


- 5 Compounds of Formula IIb can be synthesized from the corresponding thio analogue of Formula IIa by oxidation (Equation 19). Typical reagents for this type of oxidation include *m*-chloroperoxy benzoic acid, hydrogen peroxide, sodium metaperiodate, and OXONE® (potassium peroxymonosulfate).

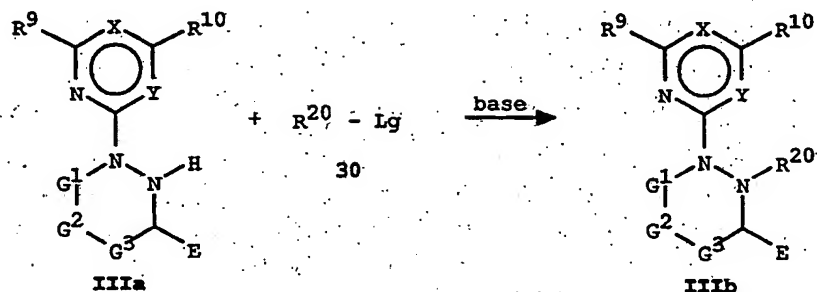
Equation 19

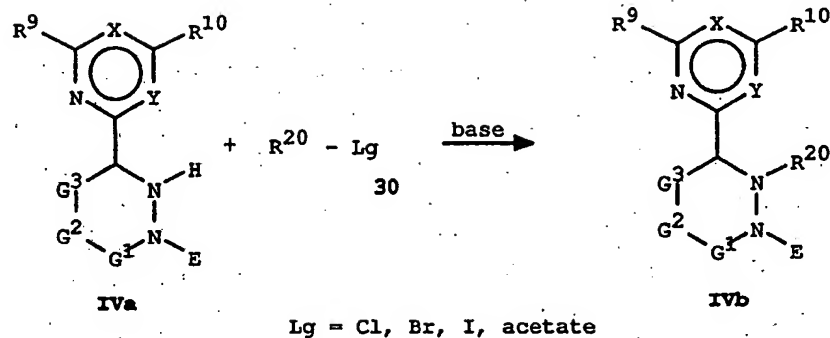


- 15 Compounds of Formulae IIIa and IVa can be prepared by reduction of compounds of Formulae I and II, respectively, with sodium borohydride/titanium (IV) chloride according to the procedure taught by Kano et al. in *Synthesis*, 1980, 695, and set forth in Equation
- 20 20. In cases where substituents in compounds of Formulae I and II are not compatible with the reduction conditions, protection and deprotection techniques, which are well-known in the art may be employed.

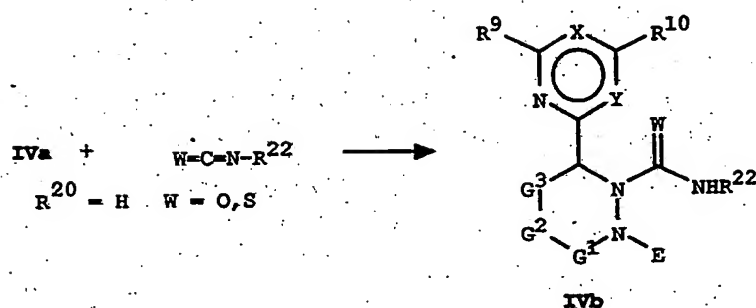
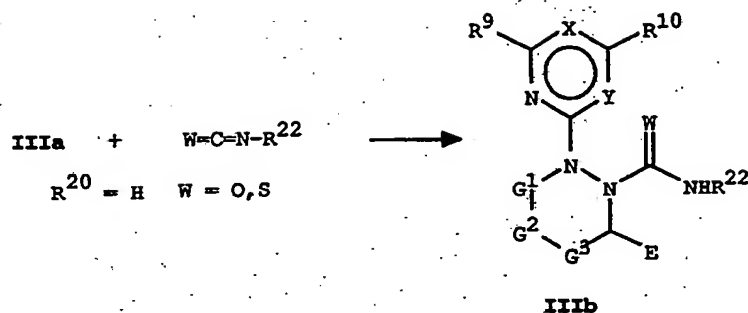
Equation 20

- 5 Compounds of Formulae IIIa and IVa can be capped on nitrogen with various substituents (R<sup>20</sup>) by treating with the appropriate alkylating, acylating, sulfonylating or phosphonylating agent of Formula 30 as shown in Equation 21. The leaving group (Lg) in
- 10 compounds of Formula 30 may be Cl, Br, I, acetate or other moiety known to act as a leaving group. Typically, these reactions are run in inert solvents such as THF, benzene or dichloromethane in the presence of a tertiary amine base, such as triethylamine, at a
- 15 temperature ranging from 0° to 100°C.

Equation 21

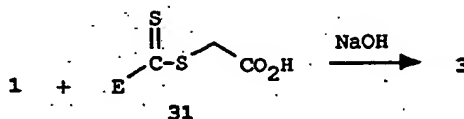


- Compounds of Formula **IIIb** and **IVb** wherein  $\text{R}^{20}$  is  $\text{C}(=\text{O})\text{NR}^{22}\text{R}^{23}$  or  $\text{C}(=\text{S})\text{NHR}^{23}$  can be prepared by treating compounds of Formulae **IIIa** or **IVa** with an isocyanate or isothiocyanate by methods well-known in the art (Equation 22). Typical solvents for this type of reaction are THF, acetonitrile and dichloromethane.

Equation 22

5

Compounds of Formula 3, as illustrated in Equation 2, can also be prepared by reacting hydrazine 1 with the appropriate carboxymethyl dithioate 31 in aqueous sodium hydroxide at 25°C (Equation 23). Carboxymethyl dithioates are known in the literature and can be prepared by one skilled in the art (see Jensen, K. A. and Pedersen, C., *Acta Chemica Scandinavica*, 1961, 15, 1087).

15 Equation 23

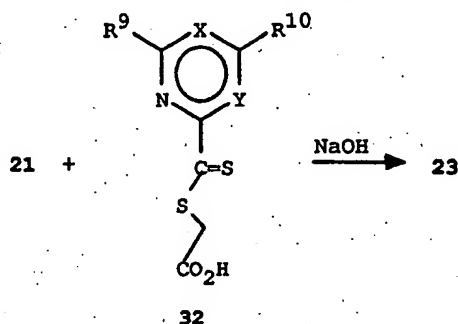
Likewise, thiohydrazides of Formula 23, as  
20 illustrated in Equation 15, can be synthesized by



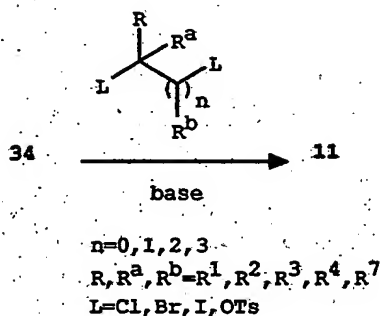
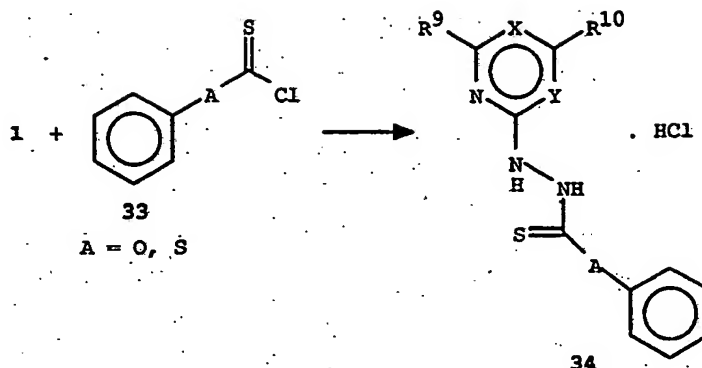
reaction of a hydrazine of Formula 21 with a carboxymethyl dithioate of Formula 32 in aqueous sodium hydroxide (Equation 24).

Equation 24

5



Compounds of Formula 11, wherein E is phenoxy or phenylthio, can also be synthesized by treating a hydrazine of Formula 1 with phenyl-chlorothionoformate or phenyl-chlorodithioformate of Formula 33 to form a thiocarbazate hydrochloride of Formula 34 (Equation 25). This type of reaction is typically run in a solvent such as methylene chloride from about -10°C to 0°C. The cyclization is performed by treating 39 with the appropriate alkylating agent in a solvent mixture of aqueous sodium hydroxide and THF at 25°C.

Equation 25

5

The metal complexes of compounds of Formulae I-IV of the instant invention include complexes with copper, zinc, iron, magnesium, or manganese. These complexes can be formed by combining the compound of Formulae I-IV with the metal salt in either aprotic solvents, such as ether or THF, or protic solvents, such as methanol. EP-A-459,662 discloses metal complexes of other nitrogen containing compounds as agricultural fungicides.

15

EXAMPLE 1

Preparation of 1-(4-ethylphenyl)-2-hydroxyethanone(4,6-dimethyl-2-pyrimidinyl)hydrazone

To a solution of 3.57 g (21.7 mmol) of *p*-ethyl-2-hydroxyacetophenone in 100 mL of acetonitrile was added 3.00 g (21.7 mmol) of 4,6-dimethyl-2-hydrazinopyrimi-

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dine, 3Å molecular sieves, and a catalytic amount of butanesulfonic acid. The reaction mixture was stirred overnight at room temperature and then diluted with dichloromethane and chloroform. The organic phase was washed successively with saturated sodium bicarbonate and brine, dried over sodium sulfate, filtered and concentrated. The crude product was passed through a plug of silica gel and triturated with hexanes to yield 3.45 g of product. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 10.65 (bs, 1H), 7.61 (d, 2H), 7.15 (d, 2H), 6.47 (s, 1H), 6.10 (bs, 1H), 4.86 (s, 2H), 2.64 (q, 2H), 2.38 (s, 6H), 1.22 (t, 3H).

#### EXAMPLE 2

##### Preparation of 3-(4,6-dimethyl-2-pyrimidinyl)-5-(4-ethylphenyl)-3,6-dihydro-2H-1,3,4-oxadiazine

A solution of 1.00 g (3.52 mmol) of 1-(4-ethylphenyl)-2-hydroxyethanone(4,6-dimethyl-2-pyrimidinyl)-hydrazone, 0.21 g (7.04 mmol) of paraformaldehyde, and a catalytic amount of butanesulfonic acid was heated at reflux for 3 h in 20 mL of acetonitrile. After cooling, the reaction mixture was diluted with dichloromethane and chloroform. The organic phase was washed successively with saturated sodium bicarbonate and brine, dried over sodium sulfate, filtered and concentrated. Chromatography on silica gel gave 70 mg of desired product as a gum. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.66 (d, 2H), 7.21 (d, 2H), 6.56 (s, 1H), 5.54 (s, 2H), 4.81 (s, 2H), 2.67 (q, 2H), 2.42 (s, 6H), 1.24 (t, 3H).

#### EXAMPLE 3

##### Preparation of 4-ethylbenzoic acid 2-(4,6-dimethyl-2-pyrimidinyl)hydrazide

4,6-Dimethyl-2-hydrazinopyrimidine (3.72 g, 26.95 mmol) was suspended in 80 mL of pyridine and the reaction mixture was cooled to 10°C. After slowly adding *p*-ethylbenzoyl chloride (5.00 g, 29.66 mmol), the reaction mixture was allowed to warm to room

temperature over 1 h. Addition of ice and water precipitated the product which was filtered and washed with hexanes to yield 6.85 g of a white solid. mp 118-119°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 9.15 (bs, 1H), 7.8 (d, 2H), 7.35 (bs, 1H), 7.2 (d, 2H), 6.52 (s, 1H), 2.7 (q, 2H), 2.33 (s, 6H), 1.23 (t, 3H).

#### EXAMPLE 4

##### Preparation of 4-(4,6-dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5,6-dihydro-4H-1,3,4-thiadiazine

10 A solution of 5.30 g (18.52 mmol) of 4-ethylbenzoic acid 2-(4,6-dimethyl-2-pyrimidinyl)hydrazide and 6.18 g (13.89 mmol) of P<sub>2</sub>S<sub>5</sub> in 60 mL of pyridine was heated at reflux for 1.5 h. After cooling, water was added and the reaction mixture was heated briefly at reflux to  
15 quench the reaction. The mixture was then cooled with an ice bath to precipitate the product. The solid was filtered and washed with water to give 6.57 g (21.73 mmol) of thiohydrazide which was then dissolved in 100 mL of THF with 7.5 mL (54.33 mmol) of triethyl-  
20 amine and 2.1 mL (23.91 mmol) of 1,2-dibromoethane. The reaction mixture was heated at reflux overnight. After cooling, water and ether were added and the organic phase was separated and washed with brine. The organic extracts were dried over magnesium sulfate,  
25 filtered and concentrated. The crude product was passed through a plug of silica gel to give 200 mg of product as an oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>), 7.8 (d, 2H), 7.2 (d, 2H), 6.53 (s, 1H), 4.45 (m, 2H), 3.35 (m, 2H), 2.67 (q, 2H), 2.41 (s, 6H), 1.22 (t, 3H).

30

#### EXAMPLE 5

##### Preparation of 4-(4,6-dimethyl-2-pyrimidinyl)-5,6-dihydro-2-(3-methylphenyl)-4H-1,3,4-oxadiazine

A solution of 1.00 g (3.89 mmol) of 3-methylbenzoic acid 2-(4,6-dimethyl-2-pyrimidinyl)hydrazide, 0.37 mL (4.28 mmol) of 1,2-dibromoethane, and 1.33 mL (8.95 mmol) of DBU in 20 mL of dry THF was heated at  
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reflux overnight. After cooling, 2.3 equivalents (8.95 mmol) of sodium hydride and 0.37 mL (4.28 mmol) of 1,2-dibromoethane were added, and the reaction mixture was heated at reflux overnight. The mixture was allowed to cool to room temperature and saturated aqueous ammonium chloride was added. The product was extracted with dichloromethane and chloroform and the organic phase was washed with brine. The organic extracts were dried over sodium sulfate, filtered, concentrated, and passed through a plug of silica gel to give 100 mg of desired product as a gum.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.82 (m, 1H), 7.75 (m, 1H), 7.25 (m, 1H), 7.19 (m, 1H), 6.49 (s, 1H), 4.54 (m, 2H), 4.28 (m, 2H), 2.42 (s, 6H), 2.38 (s, 3H).

15 EXAMPLE 6

Preparation of 4-methoxybenzenecarbothioic acid

O-[2-(4,6-dimethyl-2-pyrimidinyl)hydrazide

4,6-Dimethyl-2-hydrazinopyrimidine (p-methoxythiobenzoylthio)acetic acid (2.00 g, 14.49 mmol) and p-methoxyphenylcarboxymethyldithioate (3.48 g, 14.4 mmol) were dissolved in 20 mL of 1N aqueous sodium hydroxide and 10 mL of water. The reaction mixture was stirred at 25°C for 16 h and then acidified with 1N HCl. The resultant precipitate was filtered, washed with water, and dried under vacuum to give 3.22 g (11.2 mmol, 78%) of the title hydrazide as a white solid, m.p. 212-215°C  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  9.5 (bs, 1H), 7.85 (d, 2H), 6.95 (d, 2H), 6.57 (s, 1H), 3.87 (s, 3H), 2.39 (s, 6H).

30 EXAMPLE 7

Preparation of 4-(4,6-dimethyl-2-pyrimidinyl)-

5,6-dihydro-2-phenyl-4H-1,3,4-thiadiazine

Benzenecarbothioic acid O-[2-(4,6-dimethyl-2-pyrimidinyl)]hydrazide (0.500 g, 1.94 mmol), triethylamine (4.85 mmol, 0.67 mL) and 1,2-dibromoethane (0.44 g, 2.33 mmol) were dissolved in

10 mL of THF and heated at reflux for 5 h. After cooling, water was added and the mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate, filtered and concentrated. The product was purified by flash chromatography on silica gel to yield 0.490 g (1.73 mmol) of a solid in 89% yield, m.p. 138-142°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.88 (m, 2H), 7.37 (m, 3H), 6.55 (s, 1H), 4.47 (m, 2H), 3.36 (m, 2H), 2.42 (s, 6H).

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EXAMPLE 8

Preparation of 4-(4,6-dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5,6-dihydro-4H-1,3,4-thiadiazine 1-oxide

4-(4,6-Dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5,6-dihydro-4H-1,3,4-thiadiazine (0.800 g, 2.56 mmol) was dissolved in 10 mL of methanol and 2.5 mL of water. Sodium metaperiodate (0.600 g, 2.82 mmol) was added and the reaction mixture was heated at reflux for 1 h. Ethanol (2.5 mL) was added and heating was continued for 1 h more. The reaction mixture was then stirred at 25°C for 16 h. An additional 200 mg of sodium metaperiodate was added and the mixture was heated at reflux for 1 h. The reaction mixture was washed with water and extracted with methylene chloride. The organic layers were washed with brine, dried over sodium sulfate, and concentrated. The crude product was passed through a plug of silica gel to give 760 mg (91% yield) of a white solid, m.p. 149-164°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.95 (d, 2H), 7.28 (d, 2H), 6.7 (s, 1H), 5.45 (m, 1H), 3.9 (m, 1H), 3.4 (m, 1H), 2.85 (m, 1H), 2.7 (q, 2H), 2.49 (s, 6H), 1.26 (t, 3H).

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EXAMPLE 9

Preparation of 4-(4,6-dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5,6-dihydro-4H-1,3,4-thiadiazine 1,1-dioxide

4-(4,6-Dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5,6-dihydro-4H-1,3,4-thiadiazine 1-oxide (0.350 g,

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1.06 mmol) was dissolved in 5 mL of methanol and 2.5 mL of water. The mixture was cooled to 0°C and Oxone® (potassium peroxymonosulfate) (0.490 g, 0.80 mmol) was added. The reaction was warmed to room temperature, stirred for 1 h, then heated at reflux for 10 min. After stirring at 25°C for 16 h, water was added and the reaction mixture was extracted twice with methylene chloride. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated. The crude product was passed through a plug of silica gel to yield 350 mg (96%) of a white solid, m.p. 139-141°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.90 (d, 2H), 7.27 (d, 2H), 6.72 (s, 1H), 5.05 (m, 2H), 3.55 (m, 2H), 2.67 (q, 2H), 2.47 (s, 6H), 1.24 (t, 3H).

#### EXAMPLE 10

##### Preparation of 4-(4,6-dimethyl-2-pyrimidinyl)-5,6-dihydro-2-phenoxy-4H-1,3,4-thiadiazine

O-Phenyl 2-(4,6-dimethyl-2-pyrimidinyl)hydrazine-carbothioate hydrochloride (4.00 g, 12.74 mmol) was dissolved in 38.5 mL of 1N aqueous sodium hydroxide, 40 mL of THF, and 1.31 mL (15.29 mmol) of 1,2-dibromoethane. The reaction mixture was stirred at 25°C for 4 days. Methylene chloride was added and the reaction was washed successively with water and brine. After drying over sodium sulfate and concentrating, the crude product was passed through a plug of silica gel to give 2.48 g (8.27 mmol, 65%) of a solid, m.p. 75-85°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.31 (m, 4H), 7.18 (m, 1H), 6.47 (s, 1H), 4.39 (m, 2H), 3.29 (m, 2H), 2.36 (s, 6H).

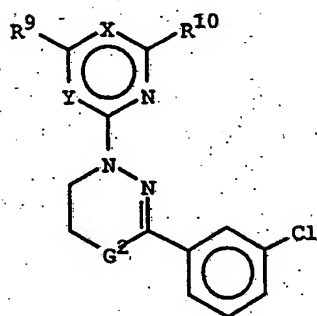
The compounds illustrated below are referred to in the tables which follow. G<sup>1</sup>, G<sup>2</sup>, G<sup>3</sup>, X, Y, E and R<sup>1</sup>-R<sup>28</sup> are as defined for compounds of Formulae I-IV in the Summary of the Invention. In addition:

n = 0-2, as in the disclosure (e.g., Equation 2);  
n<sup>1</sup> = 1-3;

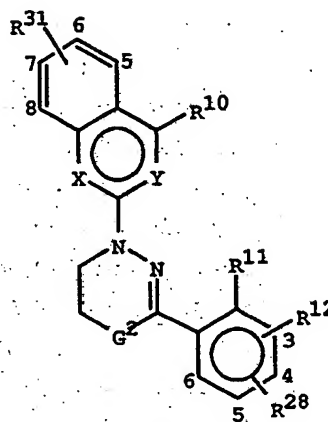
$$n^2 = 0-1;$$

$MCl_x$  = the metal chloride salts of copper, zinc, iron, magnesium, or manganese; and

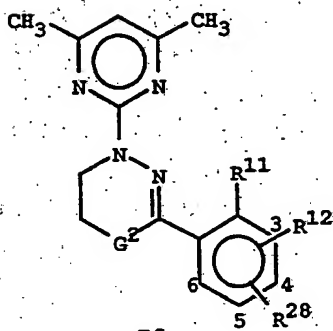
$$x = 1-2.$$



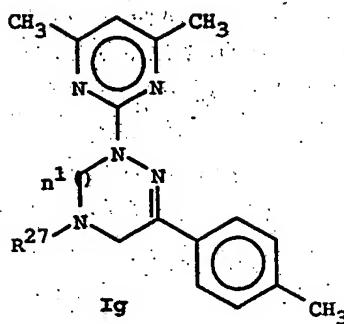
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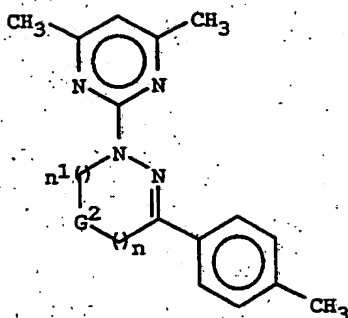
Ie



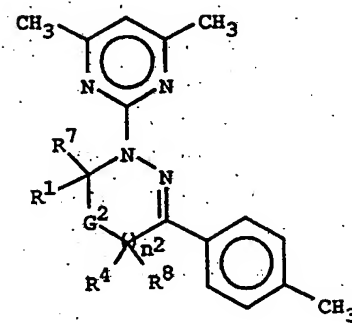
If



Ig

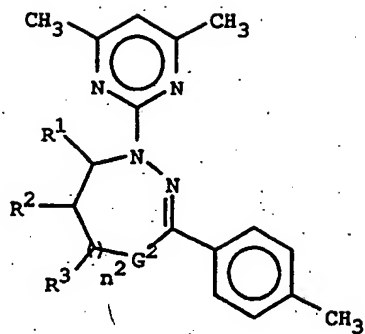


Ih

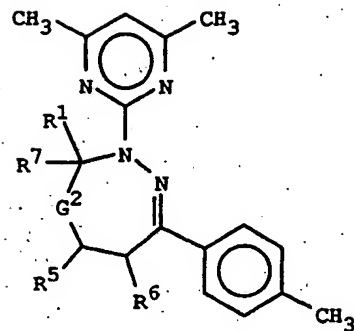


Ii

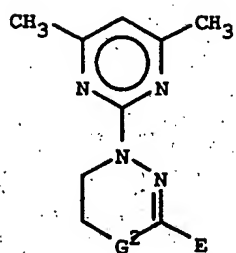




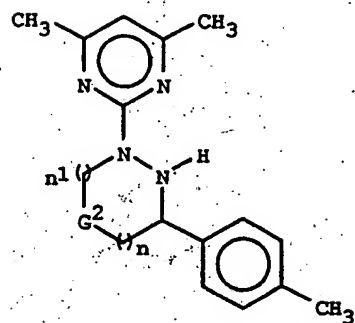
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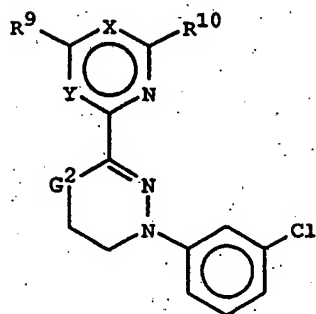
Ik



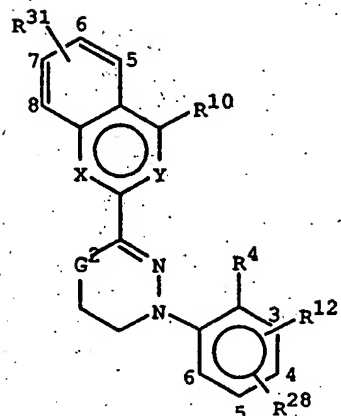
Il



IIIc

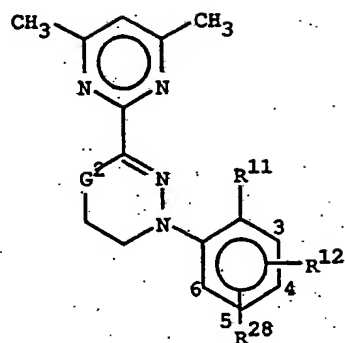


IIc

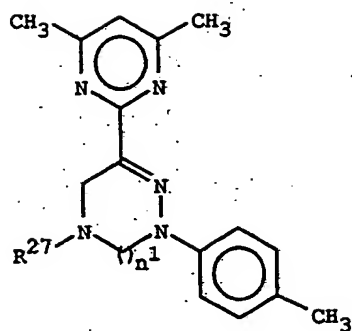


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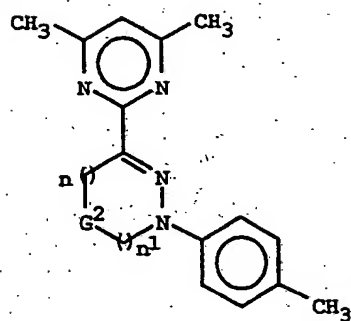
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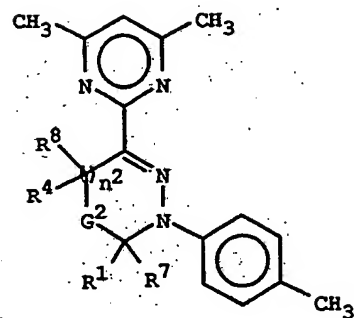
IIe



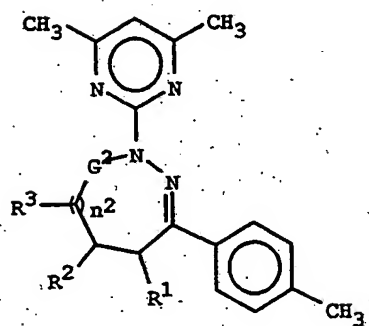
IIIf



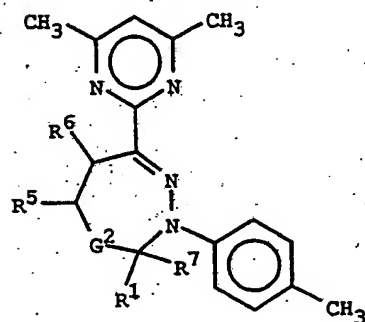
IIIf



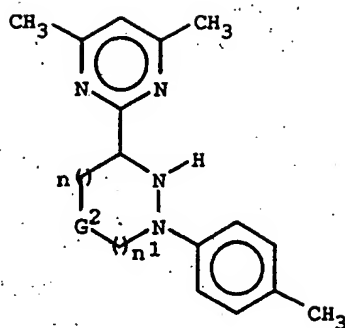
IIIf



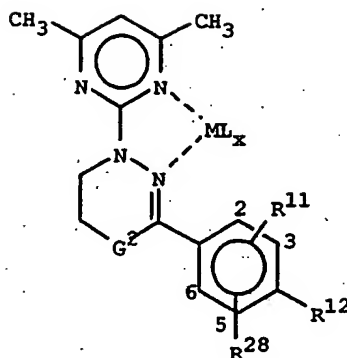
IIIf



IIIf



IVc



Im

The following abbreviations are used in the tables which follow. All alkyl groups are the normal isomers unless indicated otherwise.

t - is tertiary	t-Bu - is tertiary-butyl
s - is secondary	c-Pr - is cyclopropyl
n - is normal	c-Hex - is cyclohexyl
i - is iso	s-Bu - is secondary-butyl
c - is cyclo	OMe - is methoxy
Me - is methyl	i-PrO - is isopropoxy
Et - is ethyl	SEt - is ethylthio
Pr - is normal-propyl	CN - is cyano
Bu - is normal-butyl	TBS - is t-butyldimethylsilyl
Hex - is normal-hexyl	Ac - is acetyl
Ph - is phenyl	S(O)Me - is methylsulfinyl
Bzl - is benzyl	S(O) <sub>2</sub> Me - is methylsulfonyl
i-Pr - is isopropyl	

TABLE 1

Compounds of Formula Ia

$G^2=S$ , $R^9=Me$ , $Y=N$ ,	$OCH_2CH=CH_2$	<i>i</i> -Pr
$X=CH$	$CH_2CH_2OMe$	<i>c</i> -Pr
$R^{10}$	$OCHF_2$	<i>c</i> -Hex
H	$C=CH$	2-Me- <i>c</i> -Pr
Cl	$C=CCH_2CH_3$	$CF_3$
Br	$OCH_2C=CH$	$(CH_2)_3CF_3$
F	$NH_2$	SMe
CN	$NMe_2$	SBu
OH	NH <sub>Et</sub>	S(O)Me
Me	4-morpholinyl	S(O)Bu
Hex	pyrrolidinyl	S(O) <sub>2</sub> Me
Et	piperidinyl	S(O) <sub>2</sub> Bu
<i>i</i> -Pr	Ph	OMe
<i>c</i> -Pr	PhO	OBu
<i>c</i> -Hex	4-Me-Ph	$OCH_2CF_3$
2-Me- <i>c</i> -Pr	3- $CF_3$ -Ph	$O(CH_2)_3CF_3$
$CF_3$	4- <i>i</i> -Pr-PhO	$CH_2OMe$
$(CH_2)_3CF_3$	4-F <sub>2</sub> HCO-Ph	$(CH_2)_3OMe$
SMe	3-Et-PhO	CH=CHMe
SBu	4-MeO-PhO	CH=CHCH <sub>2</sub> CH <sub>3</sub>
S(O)Me	4-MeO-Ph	CH=CHCH <sub>2</sub> CF <sub>3</sub>
S(O)Bu		CH=CCl <sub>2</sub>
S(O) <sub>2</sub> Me	$G^2=O$ , $R^9=Me$ , $Y=N$ ,	$OCH_2CH=CH_2$
S(O) <sub>2</sub> Bu	$X=CH$	$CH_2CH_2OMe$
OMe	$R^{10}$	$OCHF_2$
OBu	H	$C=CH$
$OCH_2CF_3$	Cl	$C=CCH_2CH_3$
$O(CH_2)_3CF_3$	Br	$OCH_2C=CH$
$CH_2OMe$	F	$NH_2$
$(CH_2)_3OMe$	CN	$NMe_2$
CH=CHMe	OH	NH <sub>Et</sub>
CH=CHCH <sub>2</sub> CH <sub>3</sub>	Me	4-morpholinyl
CH=CHCH <sub>2</sub> CF <sub>3</sub>	Hex	pyrrolidinyl
CH=CCl <sub>2</sub>	Et	piperidinyl

Ph	OBu	Cl
PhO	OCH <sub>2</sub> CF <sub>3</sub>	Br
4-Me-Ph	O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	F
3-CF <sub>3</sub> -Ph	CH <sub>2</sub> OMe	CN
4- <i>i</i> -Pr-PhO	(CH <sub>2</sub> ) <sub>3</sub> OMe	OH
4-F <sub>2</sub> HCO-Ph	CH=CHMe	Me
3-Et-PhO	CH=CHCH <sub>2</sub> CH <sub>3</sub>	Hex
4-MeO-PhO	CH=CHCH <sub>2</sub> CF <sub>3</sub>	Et
4-MeO-Ph	CH=CCl <sub>2</sub>	<i>i</i> -Pr
G <sup>2</sup> =S, Y=N, X=CH,	OCH <sub>2</sub> CH=CH <sub>2</sub>	<i>c</i> -Pr
R <sup>10</sup> =H	CH <sub>2</sub> CH <sub>2</sub> OMe	<i>c</i> -Hex
R <sup>9</sup>	OCHF <sub>2</sub>	2-Me- <i>c</i> -Pr
H	C≡CH	CF <sub>3</sub>
Cl	C≡CHCH <sub>2</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
Br	OCH <sub>2</sub> C≡CH	SMe
F	NH <sub>2</sub>	SBu
CN	NMe <sub>2</sub>	S(O)Me
OH	NHEt	S(O)Bu
Me	4-morpholinyl	S(O) <sub>2</sub> Me
Hex	pyrrolidinyl	S(O) <sub>2</sub> Bu
Et	piperidinyl	OMe
<i>i</i> -Pr	Ph	OBu
<i>c</i> -Pr	PhO	OCH <sub>2</sub> CF <sub>3</sub>
<i>c</i> -Hex	4-Me-Ph	O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
2-Me- <i>c</i> -Pr	3-CF <sub>3</sub> -Ph	CH <sub>2</sub> OMe
CF <sub>3</sub>	4- <i>i</i> -Pr-PhO	(CH <sub>2</sub> ) <sub>3</sub> OMe
(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-F <sub>2</sub> HCO-Ph	CH=CHMe
SMe	3-Et-PhO	CH=CHCH <sub>2</sub> CH <sub>3</sub>
SBu	4-MeO-PhO	CH=CHCH <sub>2</sub> CF <sub>3</sub>
S(O)Me	4-MeO-Ph	CH=CCl <sub>2</sub>
S(O)Bu	G <sup>2</sup> =S, R <sup>9</sup> =R <sup>10</sup> =Me,	OCH <sub>2</sub> CH=CH <sub>2</sub>
S(O) <sub>2</sub> Me	X=CR <sup>13</sup> , Y=N	CH <sub>2</sub> CH <sub>2</sub> OMe
S(O) <sub>2</sub> Bu	R <sup>13</sup>	OCHF <sub>2</sub>
OMe	H	C≡CH
		C≡CHCH <sub>2</sub> CH <sub>3</sub>

OCH<sub>2</sub>C≡CHNH<sub>2</sub>NMe<sub>2</sub>

NHet

4-morpholinyl

pyrrolidinyl

piperidinyl

Ph

PhO

4-Me-Ph

3-CF<sub>3</sub>-Ph4-*i*-Pr-PhO4-F<sub>2</sub>HCO-Ph

3-Et-PhO

4-MeO-PhO

4-MeO-Ph

G<sup>2</sup>=S, R<sup>9</sup>=R<sup>10</sup>=Me,X=CH, Y=CR<sup>14</sup>R<sup>14</sup>

Cl

Br

F

Me

Et

OMe

OEt

H

G<sup>2</sup>=O, Y=N, X=CH,R<sup>10</sup>=HR<sup>9</sup>

H

Cl

Br

F

CN

OH

Me

Hex

Et

*i*-Pr*c*-Pr*c*-Hex2-Me-*c*-PrCF<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>

SMe

SBu

S(O)Me

S(O)Bu

S(O)<sub>2</sub>MeS(O)<sub>2</sub>Bu

OMe

OBu

OCH<sub>2</sub>CF<sub>3</sub>O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>CH<sub>2</sub>OMe(CH<sub>2</sub>)<sub>3</sub>OMe

CH=CHMe

CH=CHCH<sub>2</sub>CH<sub>3</sub>CH=CHCH<sub>2</sub>CF<sub>3</sub>CH=CCl<sub>2</sub>OCH<sub>2</sub>CH=CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OMeOCHF<sub>2</sub>

C≡CH

C≡CCH<sub>2</sub>CH<sub>3</sub>OCH<sub>2</sub>C≡CHNH<sub>2</sub>NMe<sub>2</sub>

NHet

4-morpholinyl

pyrrolidinyl

piperidinyl

Ph

PhO

4-Me-Ph

3-CF<sub>3</sub>-Ph4-*i*-Pr-PhO4-F<sub>2</sub>HCO-Ph

3-Et-PhO

4-MeO-PhO

4-MeO-Ph

G<sup>2</sup>=O, R<sup>9</sup>=R<sup>10</sup>=Me,X=CR<sup>13</sup>, Y=NR<sup>13</sup>

H

Cl

Br

F

CN

OH

Me

Hex

Et

*i*-Pr*c*-Pr*c*-Hex2-Me-*c*-PrCF<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>

SMe

SBu

S(O)Me	$G^2=O$ , $R^9=R^{10}=Me$ ,	Ph
S(O)Bu	$X=CH$ , $Y=CR^{14}$	PhO
S(O) <sub>2</sub> Me	$R^{14}$	4-Me-Ph
S(O) <sub>2</sub> Bu	Cl	4-MeO-Ph
OMe	Br	H
OBu	F	$G^2=S$ , $R^9=Me$ , $Y=CH$ ,
OCH <sub>2</sub> CF <sub>3</sub>	Me	$X=N$
O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	Et	$R^{10}$
CH <sub>2</sub> OMe	OMe	Cl
(CH <sub>2</sub> ) <sub>3</sub> OMe	OEt	Br
CH=CHMe	H	F
CH=CHCH <sub>2</sub> CH <sub>3</sub>	$G^2=S$ , $R^9=Me$ , $X=Y=N$	CN
CH=CHCH <sub>2</sub> CF <sub>3</sub>	$R^{10}$	OH
CH=CCl <sub>2</sub>	Cl	Me
OCH <sub>2</sub> CH=CH <sub>2</sub>	Br	Et
CH <sub>2</sub> CH <sub>2</sub> OMe	F	<i>i</i> -Pr
OCHF <sub>2</sub>	CN	<i>c</i> -Pr
C≡CH	OH	CF <sub>3</sub>
C≡CCH <sub>2</sub> CH <sub>3</sub>	Me	SMe
OCH <sub>2</sub> C≡CH	Et	S(O)Me
NH <sub>2</sub>	<i>i</i> -Pr	S(O) <sub>2</sub> Me
NMe <sub>2</sub>	<i>c</i> -Pr	OMe
NH <sub>2</sub> Et	CF <sub>3</sub>	OEt
4-morpholinyl	SMe	OCH <sub>2</sub> OMe
pyrrolidinyl	S(O)Me	OCH <sub>2</sub> CF <sub>3</sub>
piperidinyl	S(O) <sub>2</sub> Me	C=CHMe
Ph	OMe	C≡CMe
PhO	OEt	NMe <sub>2</sub>
4-Me-Ph	OCH <sub>2</sub> OMe	Ph
3-CF <sub>3</sub> -Ph	OCH <sub>2</sub> CF <sub>3</sub>	PhO
4- <i>i</i> -Pr-PhO	C=CHMe	4-Me-Ph
4-F <sub>2</sub> HCO-Ph	C≡CMe	4-MeO-Ph
3-Et-PhO	NMe <sub>2</sub>	H
4-MeO-PhO		
4-MeO-Ph		

$G^2=O$ ,  $R^9=Me$ ,  $X=Y=N$  $R^{10}$ 

Cl

Br

F

CN

OH

Me

Et

*i*-Pr*c*-Pr $CF_3$ 

SMe

S(O)Me

S(O)<sub>2</sub>Me

OMe

OEt

OCH<sub>2</sub>OMeOCH<sub>2</sub>CF<sub>3</sub>

C=CHMe

C=Me

NMe<sub>2</sub>

Ph

PhO

4-Me-Ph

4-MeO-Ph

H

 $G^2=O$ ,  $R^9=Me$ ,  $Y=CH$ ,

X=N

 $R^{10}$ 

Cl

Br

F

CN

OH

Me

Et

*i*-Pr*c*-Pr $CF_3$ 

SMe

S(O)Me

S(O)<sub>2</sub>Me

OMe

OEt

OCH<sub>2</sub>OMeOCH<sub>2</sub>CF<sub>3</sub>

C=CHMe

C=Me

NMe<sub>2</sub>

Ph

PhO

4-Me-Ph

4-MeO-Ph

H

 $G^2=S$ 

X

Y

 $R^{14}$  $R^9$  $R^{13}$  $R^{10}$ 

N

CR<sup>14</sup>-(CH<sub>2</sub>)<sub>3</sub>-

---

Me

CH

CR<sup>14</sup>-(CH<sub>2</sub>)<sub>3</sub>-

---

Me

N

CR<sup>14</sup>-(CH<sub>2</sub>)<sub>4</sub>-

---

Me

CH

CR<sup>14</sup>-(CH<sub>2</sub>)<sub>4</sub>-

---

Me

CR<sup>13</sup>

N

---

-(CH<sub>2</sub>)<sub>3</sub>-

---

Me

CR<sup>13</sup>

CH

---

-(CH<sub>2</sub>)<sub>3</sub>-

---

Me

CR<sup>13</sup>

N

---

-(CH<sub>2</sub>)<sub>4</sub>-

---

Me

CR<sup>13</sup>

CH

---

-(CH<sub>2</sub>)<sub>4</sub>-

---

Me

CR<sup>13</sup>

CH

---

Me

-(CH<sub>2</sub>)<sub>3</sub>-CR<sup>13</sup>

CH

---

Me

-(CH<sub>2</sub>)<sub>4</sub>-



$G^2=O$						
X	Y	$R^{14}$	$R^9$	$R^{13}$	$R^{10}$	
N	$CR^{14}$	$-(CH_2)_3-$		--	Me	
CH	$CR^{14}$	$-(CH_2)_3-$		--	Me	
N	$CR^{14}$	$-(CH_2)_4-$		--	Me	
CH	$CR^{14}$	$-(CH_2)_4-$		--	Me	
$CR^{13}$	N	--	$-(CH_2)_3-$		Me	
$CR^{13}$	CH	--	$-(CH_2)_3-$		Me	
$CR^{13}$	N	--	$-(CH_2)_4-$		Me	
$CR^{13}$	CH	--	$-(CH_2)_4-$		Me	
$CR^{13}$	CH	--	Me	$-(CH_2)_3-$		
$CR^{13}$	CH	--	Me	$-(CH_2)_4-$		

TABLE 2

Compounds of Formula Ia

 $G^2=S$ ,  $X=Y=N$ ,  $R^{11}=R^{12}=R^{28}=H$ 

$R^{10}$		
Cl	c-Pr	C=CHMe
Br	$CF_3$	C=CMe
F	SMe	NMe <sub>2</sub>
CN	S(O)Me	Ph
OH	S(O) <sub>2</sub> Me	PhO
Me	OMe	4-Me-Ph
Et	OEt	4-MeO-Ph
i-Pr	OCH <sub>2</sub> OMe	H
	OCH <sub>2</sub> CF <sub>3</sub>	

$G^2=S$						
X	Y	$R^{10}$	$R^{11}$	$R^{12}$	$R^{28}$	$R^{31}$
CH	N	Me	H	H	H	H
N	CH	Me	H	H	H	H
N	N	Me	H	3-Me	4-Me	H
N	N	Me	H	3-Me	4-Me	6-Me
N	N	Me	Me	H	H	7-Me

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N	N	Me	H	H	4- <i>i</i> -Pr	6-OMe
N	N	Me	H	3-Me	H	7-CF <sub>3</sub>
N	N	Me	H	H	4-Et	7-Et
N	N	Me	H	H	4- <i>i</i> -Pr	6-OCHF <sub>2</sub>
N	N	Me	H	H	H	8-Bu
N	N	Me	H	H	4- <i>c</i> -Pr	6-OEt

G<sup>2</sup>=O, X=Y=N, R<sup>11</sup>=R<sup>12</sup>=R<sup>28</sup>=H

R <sup>10</sup>	<i>c</i> -Pr	C=CHMe
Cl	CF <sub>3</sub>	C=OMe
Br	SMe	NMe <sub>2</sub>
F	S(O)Me	Ph
CN	S(O) <sub>2</sub> Me	PhO
OH	OMe	4-Me-Ph
Me	OEt	4-MeO-Ph
Et	OCH <sub>2</sub> OMe	H
<i>i</i> -Pr	OCH <sub>2</sub> CF <sub>3</sub>	

G<sup>2</sup>=O

X	Y	R <sup>10</sup>	R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>	R <sup>31</sup>
CH	N	Me	H	H	H	H
N	CH	Me	H	H	H	H
N	N	Me	H	3-Me	4-Me	H
N	N	Me	H	3-Me	4-Me	6-Me
N	N	Me	Me	H	H	7-Me
N	N	Me	H	H	4- <i>i</i> -Pr	6-OMe
N	N	Me	H	3-Me	H	7-CF <sub>3</sub>
N	N	Me	H	H	4-Et	7-Et
N	N	Me	H	H	4- <i>i</i> -Pr	6-OCHF <sub>2</sub>
N	N	Me	H	H	H	8-Bu
N	N	Me	H	H	4- <i>c</i> -Pr	6-OEt

TABLE 3

Compounds of Formula I f

$G^2=S$ , $R^{12}=H$ , $R^{28}=H$ $R^{11}$	$G^2=S$ , $R^{11}=R^{12}=H$ $R^{28}$	$4-C\equiv CH$
H	4-Me	$4-C\equiv C-Et$
Me	4-CN	$4-OCH_2C\equiv CH$
Et	4-NO <sub>2</sub>	4-NMe <sub>2</sub>
<i>i</i> -Pr	4-OH	$4-C(=O)NMe_2$
<i>s</i> -Bu	4-CO <sub>2</sub> H	4-Ph
F	4-CO <sub>2</sub> Et	4-OPh
Cl	4-Et	4-SPh
Br	4- <i>i</i> -Pr	4-(3-Me-Ph)
CF <sub>3</sub>	4- <i>n</i> -Hex	
OMe	4- <i>c</i> -Pr	$G^2=S$
OEt	4-CF <sub>3</sub>	$R^{11}$ $R^{12}$ $R^{28}$
OCHF <sub>2</sub>	4-SMe	Cl H 6-Cl
OBu	4-SBu	H 3-Me 4-Me
O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4- <i>c</i> -Hex	H 3-Me 4-Et
(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-Cl	H 3-OMe 4-OMe
$G^2=S$ , $R^{11}=H$ , $R^{28}=H$ $R^{12}$	4-Br	Me H 5-Me
3-Me	4-F	Me H 4-Me
3-Et	4-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	Me 4-Me 5-Me
3- <i>i</i> -Pr	4-S(O)Me	H 3-Cl 5-Cl
3- <i>s</i> -Bu	4-S(O)Bu	Cl H 4-Cl
3-F	4-S(O) <sub>2</sub> Me	
3-Cl	4-S(O) <sub>2</sub> Bu	$G^2=O$ , $R^{12}=H$ , $R^{28}=H$
3-Br	4-OMe	$R^{11}$
3-CF <sub>3</sub>	4-OBu	H
3-OMe	4-OCH <sub>2</sub> CF <sub>3</sub>	Me
3-OEt	4-OCH <sub>2</sub> OMe	Et
3-OCHF <sub>2</sub>	4-CH <sub>2</sub> OMe	<i>i</i> -Pr
3-OBu	4-CH=CH-Me	<i>s</i> -Bu
3-O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-CH=CHCH <sub>2</sub> Me	F
3-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-TBS	Cl
	4-SiMe <sub>3</sub>	Br
		CF <sub>3</sub>

OMe  
OEt  
OCHF<sub>2</sub>  
OBu  
O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
G<sup>2</sup>=O, R<sup>11</sup>=H, R<sup>28</sup>=H  
R<sup>12</sup>  
3-Me  
3-Et  
3-*i*-Pr  
3-*s*-Bu  
3-F  
3-Cl  
3-Br  
3-CF<sub>3</sub>  
3-OMe  
3-OEt  
3-OCHF<sub>2</sub>  
3-OBu  
3-O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
3-(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
G<sup>2</sup>=O, R<sup>11</sup>=R<sup>12</sup>=H  
R<sup>28</sup>  
4-Me  
4-CN  
4-NO<sub>2</sub>  
4-OH  
4-CO<sub>2</sub>H  
4-CO<sub>2</sub>Et  
4-Et  
4-*i*-Pr  
4-*n*-Hex

4-*c*-Pr  
4-CF<sub>3</sub>  
4-SMe  
4-SBu  
4-*c*-Hex  
4-Cl  
4-Br  
4-F  
4-(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
4-S(O)Me  
4-S(O)Bu  
4-S(O)<sub>2</sub>Me  
4-S(O)<sub>2</sub>Bu  
4-OMe  
4-OBu  
4-OCH<sub>2</sub>CF<sub>3</sub>  
4-OCH<sub>2</sub>OMe  
4-CH<sub>2</sub>OMe  
4-CH=CH-Me  
4-CH=CHCH<sub>2</sub>Me  
4-TBS  
4-SiMe<sub>3</sub>  
4-C≡CH  
4-C≡C-Et  
4-OCH<sub>2</sub>C≡CH  
4-NMe<sub>2</sub>  
4-C(=O)NMe<sub>2</sub>  
4-Ph  
4-OPh  
4-SPh  
4-(3-Me-Ph)  
G<sup>2</sup>=O  
R<sup>11</sup> R<sup>12</sup> R<sup>28</sup>  
Cl H 6-Cl

H 3-Me 4-Me  
H 3-Me 4-Et  
H 3-OMe 4-OMe  
Me H 5-Me  
Me H 4-Me  
Me 4-Me 5-Me  
H 3-Cl 5-Cl  
Cl H 4-Cl  
G<sup>2</sup>=S(O), R<sup>12</sup>=H,  
R<sup>28</sup>=H  
R<sup>11</sup>  
H  
Me  
Et  
*i*-Pr  
*s*-Bu  
F  
Cl  
Br  
CF<sub>3</sub>  
OMe  
OEt  
OCHF<sub>2</sub>  
OBu  
O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
G<sup>2</sup>=S(O), R<sup>11</sup>=H,  
R<sup>28</sup>=H  
R<sup>12</sup>  
3-Me  
3-Et  
3-*i*-Pr  
3-*s*-Bu

3-F  
 3-Cl  
 3-Br  
 3-CF<sub>3</sub>  
 3-OMe  
 3-OEt  
 3-OCHF<sub>2</sub>  
 3-OBu  
 3-O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 3-(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 G<sup>2</sup>=S(O), R<sup>11</sup>=R<sup>12</sup>=H  
 R<sup>28</sup>  
 4-Me  
 4-CN  
 4-NO<sub>2</sub>  
 4-OH  
 4-CO<sub>2</sub>H  
 4-CO<sub>2</sub>Et  
 4-Et  
 4-*i*-Pr  
 4-*n*-Hex  
 4-*c*-Pr  
 4-CF<sub>3</sub>  
 4-SMe  
 4-SBu  
 4-*c*-Hex  
 4-Cl  
 4-Br  
 4-F  
 4-(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 4-S(O)Me  
 4-S(O)Bu  
 4-S(O)<sub>2</sub>Me  
 4-S(O)<sub>2</sub>Bu

4-OMe  
 4-OBu  
 4-OCH<sub>2</sub>CF<sub>3</sub>  
 4-OCH<sub>2</sub>OMe  
 4-CH<sub>2</sub>OMe  
 4-CH=CH-Me  
 4-CH=CHCH<sub>2</sub>Me  
 4-TBS  
 4-SiMe<sub>3</sub>  
 4-C≡CH  
 4-C≡C-Et  
 4-OCH<sub>2</sub>C≡CH  
 4-NMe<sub>2</sub>  
 4-C(=O)NMe<sub>2</sub>  
 4-Ph  
 4-OPh  
 4-SPh  
 4-(3-Me-Ph)

G<sup>2</sup>=S(O)  
 R<sup>11</sup> R<sup>12</sup> R<sup>28</sup>  
 Cl H 6-Cl  
 H 3-Me 4-Me  
 H 3-Me 4-Et  
 H 3-OMe 4-OMe  
 Me H 5-Me  
 Me H 4-Me  
 Me 4-Me 5-Me  
 H 3-Cl 5-Cl  
 Cl H 4-Cl

G<sup>2</sup>=S(O)<sub>2</sub>, R<sup>12</sup>=H,  
 R<sup>28</sup>=H  
 R<sup>11</sup>  
 H

Me  
 Et  
*i*-Pr  
*s*-Bu  
 F  
 Cl  
 Br  
 CF<sub>3</sub>  
 OMe  
 OEt  
 OCHF<sub>2</sub>  
 OBU  
 O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 (CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 G<sup>2</sup>=S(O)<sub>2</sub>, R<sup>11</sup>=H,  
 R<sup>28</sup>=H  
 R<sup>12</sup>  
 3-Me  
 3-Et  
 3-*i*-Pr  
 3-*s*-Bu  
 3-F  
 3-Cl  
 3-Br  
 3-CF<sub>3</sub>  
 3-OMe  
 3-OEt  
 3-OCHF<sub>2</sub>  
 3-OBu  
 3-O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 3-(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>

G<sup>2</sup>=S(O)<sub>2</sub>,R<sup>11</sup>=R<sup>12</sup>=HR<sup>28</sup>

4-Me

4-CN

4-NO<sub>2</sub>

4-OH

4-CO<sub>2</sub>H4-CO<sub>2</sub>Et

4-Et

4-*i*-Pr4-*n*-Hex4-*c*-Pr4-CF<sub>3</sub>

4-SMe

4-SBu

4-*c*-Hex

4-Cl

4-Br

4-F

4-(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>

4-S(O)Me

4-S(O)Bu

4-S(O)<sub>2</sub>Me4-S(O)<sub>2</sub>Bu

4-OMe

4-OBu

4-OCH<sub>2</sub>CF<sub>3</sub>4-OCH<sub>2</sub>OMe4-CH<sub>2</sub>OMe

4-CH=CH-Me

4-CH=CHCH<sub>2</sub>Me

4-TBS

4-SiMe<sub>3</sub>

4-C≡CH

4-C≡C-Et

4-OCH<sub>2</sub>C≡CH4-NMe<sub>2</sub>4-C(=O)NMe<sub>2</sub>

4-Ph

4-OPh

4-SPh

4-(3-Me-Ph)

G<sup>2</sup>=S(O)<sub>2</sub>R<sup>11</sup> R<sup>12</sup> R<sup>28</sup>

Cl H 6-Cl

H 3-Me 4-Me

H 3-Me 4-Et

H 3-OMe 4-OMe

Me H 5-Me

Me H 4-Me

Me 4-Me 5-Me

H 3-Cl 5-Cl

Cl H 4-Cl

TABLE 4

Compounds of Formula Ig

$n^1=1$	Et
$R^{27}$	Bu
H	<i>i</i> -Pr
Et	CHF <sub>2</sub>
Bu	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
<i>i</i> -Pr	CO <sub>2</sub> Et
CHF <sub>2</sub>	C(=O)Me
(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	C(=O)(CH <sub>2</sub> ) <sub>3</sub> Me
CO <sub>2</sub> Et	C(=O)Ph
C(=O)Me	(3-Me-Ph)C(=O)
C(=O)(CH <sub>2</sub> ) <sub>3</sub> Me	(4-OMe-Ph)C(=O)
C(=O)Ph	CH <sub>2</sub> C=CH <sub>2</sub>
(3-Me-Ph)C(=O)	CH <sub>2</sub> C=CH
(4-OMe-Ph)C(=O)	PhCH <sub>2</sub>
CH <sub>2</sub> C=CH <sub>2</sub>	4-Me-PhCH <sub>2</sub>
CH <sub>2</sub> C=CH	S(O) <sub>2</sub> Me
PhCH <sub>2</sub>	C(=O)NMe <sub>2</sub>
4-Me-PhCH <sub>2</sub>	C(=S)NHMe
S(=O) <sub>2</sub> Me	S(O)Me
C(=O)NMe <sub>2</sub>	S(O) <sub>2</sub> Ph
C(=S)NHMe	(4-Me-Ph)S(O) <sub>2</sub>
S(O)Me	C(=O)NHPh
S(O) <sub>2</sub> Ph	C(=S)NHPh
(4-Me-Ph)S(O) <sub>2</sub>	P(=S)(OEt) <sub>2</sub>
C(=O)NHPh	P(=O)(OEt) <sub>2</sub>
C(=S)NHPh	S(O) <sub>2</sub> N(Et) <sub>2</sub>
P(=S)(OEt) <sub>2</sub>	
P(=O)(OEt) <sub>2</sub>	$n^1=3$
S(O) <sub>2</sub> N(Et) <sub>2</sub>	$R^{27}$
$n^1=2$	H
	Et
$R^{27}$	Bu
H	<i>i</i> -Pr

$\text{CHF}_2$   
 $(\text{CH}_2)_3\text{CF}_3$   
 $\text{CO}_2\text{Et}$   
 $\text{C}(=\text{O})\text{Me}$   
 $\text{C}(=\text{O})(\text{CH}_2)_3\text{Me}$   
 $\text{C}(=\text{O})\text{Ph}$   
 $(3\text{-Me-Ph})\text{C}(=\text{O})$   
 $(4\text{-OMe-Ph})\text{C}(=\text{O})$   
 $\text{CH}_2\text{C}=\text{CH}_2$   
 $\text{CH}_2\text{C}\equiv\text{CH}$   
 $\text{PhCH}_2$   
 $4\text{-Me-PhCH}_2$   
 $\text{S}(\text{O})_2\text{Me}$   
 $\text{C}(=\text{O})\text{NMe}_2$   
 $\text{C}(=\text{S})\text{NHMe}$   
 $\text{S}(\text{O})\text{Me}$   
 $\text{S}(\text{O})_2\text{Ph}$   
 $(4\text{-Me-Ph})\text{S}(\text{O})_2$   
 $\text{C}(=\text{O})\text{NHPh}$   
 $\text{C}(=\text{S})\text{NHPh}$   
 $\text{P}(=\text{S})(\text{OEt})_2$   
 $\text{P}(=\text{O})(\text{OEt})_2$   
 $\text{S}(\text{O})_2\text{N}(\text{Et})_2$

TABLE 5

Compounds of Formula Ia

n	n <sup>1</sup>	G <sup>2</sup>
1	1	S
1	2	S
2	1	S
0	3	S
1	1	O
1	2	O
2	1	O
0	3	O

1	1	S(O)
1	2	S(O)
2	1	S(O)
0	3	S(O)
1	1	S(O) <sub>2</sub>
1	2	S(O) <sub>2</sub>
2	1	S(O) <sub>2</sub>
0	3	S(O) <sub>2</sub>
1	1	N-Me
1	2	N-Me
2	1	N-Me

TABLE 6

Compounds of Formula II

G<sup>2</sup>=S

n <sup>2</sup>	R <sup>1</sup>	R <sup>7</sup>	R <sup>4</sup>	R <sup>8</sup>
1	Me	H	H	H
1	Bu	H	H	H
1	Me	Me	H	H
1	H	H	Me	H
1	H	H	Bu	H
1	Ph	H	H	H
1	4-Me-Ph	H	H	H
1	4-OMe-Ph	H	H	H
0	Me	H	--	--
0	Bu	H	--	--
0	Me	Me	--	--
0	Ph	H	--	--
0	4-Me-Ph	H	--	--

G<sup>2</sup>=O

n <sup>2</sup>	R <sup>1</sup>	R <sup>7</sup>	R <sup>4</sup>	R <sup>8</sup>
1	Me	H	H	H
1	Bu	H	H	H
1	Me	Me	H	H



1	H	H	Me	H
1	H	H	Bu	H
1	Ph	H	H	H
1	4-Me-Ph	H	H	H
1	4-OMe-Ph	H	H	H
0	Me	H	--	--
0	Bu	H	--	--
0	Me	Me	--	--
0	Ph	H	--	--
0	4-Me-Ph	H	--	--

TABLE 7

Compounds of Formula Ij

$G^2=S$				
$n^2$	$R^1$	$R^2$	$R^3$	
0	Me	H	--	
0	Bu	H	--	
0	H	Me	--	
0	H	Bu	--	
0	Ph	H	--	
0	4-Me-Ph	H	--	
0	H	4-OMe-Ph	--	
1	Me	H	H	
1	Bu	H	H	
1	H	Me	H	
1	H	Bu	H	
1	H	H	Me	
1	H	H	Bu	
1	Ph	H	H	

1	4-Me-Ph	H	H
1	H	Ph	H
1	H	4-Me-Ph	H
1	H	H	Ph
1	H	H	4-Me-Ph

 $G^2=O$ 

$n^2$	$R^1$	$R^2$	$R^3$
0	Me	H	--
0	Bu	H	--
0	H	Me	--
0	H	Bu	--
0	Ph	H	--
0	4-Me-Ph	H	--
0	H	4-OMe-Ph	--
1	Me	H	H
1	Bu	H	H
$n^2$	$R^1$	$R^2$	$R^3$
1	H	Me	H
1	H	Bu	H
1	H	H	Me
1	H	H	Bu
1	Ph	H	H
$n^2$	$R^1$	$R^2$	$R^3$
1	4-Me-Ph	H	H
1	H	Ph	H
1	H	4-Me-Ph	H
1	H	H	Ph
1	H	H	4-Me-Ph

TABLE 8

Compounds of Formula Ik

$G^2=S$					H	H	Ph	H
$R^1$	$R^7$	$R^5$	$R^6$		H	H	H	Me
H	H	Me	H		H	H	H	Ph

Me	H	H	H	Ph	H	H	H
Me	Me	H	H	H	Ph	H	H
Ph	H	H	H	H	H	Bu	H
H	Ph	H	H	H	H	4-Me-Ph	H
H	H	Bu	H	H	H	H	Bu
H	H	4-Me-Ph	H	H	H	H	4-OMe-Ph
H	H	H	Bu	Bu	H	H	H
H	H	H	4-OMe-Ph	3-Me-Ph	H	H	H
Bu	H	H	H	4-OMe-Ph	H	H	H
3-Me-Ph	H	H	H				
4-OMe-Ph	H	H	H				
G <sup>2</sup> -O							
R <sup>1</sup>	R <sup>7</sup>	R <sup>5</sup>	R <sup>6</sup>				
H	H	Me	H				
H	H	Ph	H				
H	H	H	Me				
H	H	H	Ph				
Me	H	H	H				
Me	Me	H	H				

TABLE 9

## Compounds of Formula II

G <sup>2</sup> -S	3-thienyl
E	2,5-diMe-3-furanyl
H	2,5-diMe-3-thienyl
Me	4-Me-PhO
n-Hex	2-Cl-PhO
c-Hex	2,6-diMe-PhO
PhCH <sub>2</sub>	4-Me-PhNH
CH <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	3-Me-PhS
OBu	s-BuS
O(CH <sub>2</sub> ) <sub>5</sub> Cl	1-indanyl
1-naphthalenyl	5-Me-2-thienyl
2-naphthalenyl	5-Me-2-pyridyl
2-furanyl	4-Me-3-furanyl

2-Me-3-pyridyl

 $G^2=O$ 

E

H

Me

*n*-Hex*c*-HexPhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub>

OBu

O(CH<sub>2</sub>)<sub>5</sub>Cl

1-naphthalenyl

2-naphthalenyl

2-furanyl

3-thienyl

2,5-diMe-3-furanyl

2,5-diMe-3-thienyl

4-Me-PhO

2-Cl-PhO

2,6-diMe-PhO

4-Me-PhNH

3-Me-PhS

*s*-BuS

1-indanyl

5-Me-2-thienyl

5-Me-2-pyridyl

4-Me-3-furanyl

2-Me-3-pyridyl

 $G^2=S(O)$ 

E

H

Me

*n*-Hex*c*-HexPhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub>

OBu

O(CH<sub>2</sub>)<sub>5</sub>Cl

1-naphthalenyl

2-naphthalenyl

2-furanyl

3-thienyl

2,5-diMe-3-furanyl

2,5-diMe-3-thienyl

4-Me-PhO

2-Cl-PhO

2,6-diMe-PhO

4-Me-PhNH

3-Me-PhS

*s*-BuS

1-indanyl

5-Me-2-thienyl

5-Me-2-pyridyl

4-Me-3-furanyl

2-Me-3-pyridyl

 $G^2=S(O)_2$ 

E

H

Me

*n*-Hex*c*-HexPhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub>

OBu

O(CH<sub>2</sub>)<sub>5</sub>Cl

1-naphthalenyl

2-naphthalenyl

2-furanyl	3-Me-PhS
3-thienyl	s-BuS
2,5-diMe-3-furanyl	1-indanyl
2,5-diMe-3-thienyl	5-Me-2-thienyl
4-Me-PhO	5-Me-2-pyridyl
2-Cl-PhO	4-Me-3-furanyl
2,6-diMe-PhO	2-Me-3-pyridyl
4-Me-PhNH	

TABLE 10

Compounds of Formula IIIc

G <sup>2</sup>	n	n <sup>1</sup>	S(O)	1	1
S	0	1	S(O)	1	2
S	0	2	S(O)	2	1
S	0	3	S(O) <sub>2</sub>	0	1
S	1	1	S(O) <sub>2</sub>	0	2
S	1	2	S(O) <sub>2</sub>	0	3
S	2	1	S(O) <sub>2</sub>	1	1
O	0	1	S(O) <sub>2</sub>	1	2
O	0	2	S(O) <sub>2</sub>	2	1
O	0	3	NMe	0	1
O	1	1	NMe	0	2
O	1	2	NMe	0	3
O	2	1	NMe	1	1
S(O)	0	1	NMe	1	2
S(O)	0	2	NMe	2	1
S(O)	0	3			

TABLE 11

Compounds of Formula IIc

G <sup>2</sup> =S, R <sup>9</sup> =Me, Y=N,	Br	Hex
X=CH	F	Et
R <sup>10</sup>	CN	i-Pr
H	OH	c-Pr
Cl	Me	c-Hex

2-Me-c-Pr

CF<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>

SMe

SBu

S(O)Me

S(O)Bu

S(O)<sub>2</sub>MeS(O)<sub>2</sub>Bu

OMe

OBu

OCH<sub>2</sub>CF<sub>3</sub>O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>CH<sub>2</sub>OMe(CH<sub>2</sub>)<sub>3</sub>OMe

CH=CHMe

CH=CHCH<sub>2</sub>CH<sub>3</sub>CH=CHCH<sub>2</sub>CF<sub>3</sub>CH=CCl<sub>2</sub>OCH<sub>2</sub>CH=CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OMeOCHF<sub>2</sub>

C≡CH

C≡CCH<sub>2</sub>CH<sub>3</sub>OCH<sub>2</sub>C≡CHNH<sub>2</sub>NMe<sub>2</sub>

NHET

4-morpholinyl

pyrrolidinyl

piperidinyl

Ph

PhO

4-Me-Ph

3-CF<sub>3</sub>-Ph

4-i-Pr-PhO

4-F<sub>2</sub>HCO-Ph

3-Et-PhO

4-MeO-PhO

4-MeO-Ph

G<sup>2</sup>=O, R<sup>9</sup>=Me, Y=N,

X=CH

R<sup>10</sup>

H

Cl

Br

F

CN

OH

Me

Hex

Et

i-Pr

c-Pr

c-Hex

2-Me-c-Pr

CF<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>

SMe

SBu

S(O)Me

S(O)Bu

S(O)<sub>2</sub>MeS(O)<sub>2</sub>Bu

OMe

OBu

OCH<sub>2</sub>CF<sub>3</sub>O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>CH<sub>2</sub>OMe(CH<sub>2</sub>)<sub>3</sub>OMe

CH=CHMe

CH=CHCH<sub>2</sub>CH<sub>3</sub>CH=CHCH<sub>2</sub>CF<sub>3</sub>CH=CCl<sub>2</sub>OCH<sub>2</sub>CH=CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OMeOCHF<sub>2</sub>

C≡CH

C≡CCH<sub>2</sub>CH<sub>3</sub>OCH<sub>2</sub>C≡CHNH<sub>2</sub>NMe<sub>2</sub>

NHET

4-morpholinyl

pyrrolidinyl

piperidinyl

Ph

PhO

4-Me-Ph

3-CF<sub>3</sub>-Ph

4-i-Pr-PhO

4-F<sub>2</sub>HCO-Ph

3-Et-PhO

4-MeO-PhO

4-MeO-Ph

G<sup>2</sup>=S, Y=N, X=CH,R<sup>10</sup>=HR<sup>9</sup>

H

Cl

Br

F

CN

OH	4-morpholinyl	S(O) <sub>2</sub> Me
Me	pyrrolidinyl	S(O) <sub>2</sub> Bu
Hex	piperidinyl	OMe
Et	Ph	OBu
<i>i</i> -Pr	PhO	OCH <sub>2</sub> CF <sub>3</sub>
<i>c</i> -Pr	4-Me-Ph	O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
<i>c</i> -Hex	3-CF <sub>3</sub> -Ph	CH <sub>2</sub> OMe
2-Me- <i>c</i> -Pr	4- <i>i</i> -Pr-PhO	(CH <sub>2</sub> ) <sub>3</sub> OMe
CF <sub>3</sub>	4-F <sub>2</sub> HCO-Ph	CH=CHMe
(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	3-Et-PhO	CH=CHCH <sub>2</sub> CH <sub>3</sub>
SMe	4-MeO-PhO	CH=CHCH <sub>2</sub> CF <sub>3</sub>
SBu	4-MeO-Ph	CH=CCl <sub>2</sub>
S(O)Me		OCH <sub>2</sub> CH=CH <sub>2</sub>
S(O)Bu	G <sup>2</sup> =S, R <sup>9</sup> =R <sup>10</sup> =Me,	CH <sub>2</sub> CH <sub>2</sub> OMe
S(O) <sub>2</sub> Me	X=CR <sup>13</sup> , Y=N	OCHF <sub>2</sub>
S(O) <sub>2</sub> Bu	R <sup>13</sup>	C≡CH
OMe	H	C≡CCH <sub>2</sub> CH <sub>3</sub>
OBu	Cl	OCH <sub>2</sub> C≡CH
OCH <sub>2</sub> CF <sub>3</sub>	Br	NH <sub>2</sub>
O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	F	NMe <sub>2</sub>
CH <sub>2</sub> OMe	CN	NH <sub>2</sub> Et
(CH <sub>2</sub> ) <sub>3</sub> OMe	OH	4-morpholinyl
CH=CHMe	Me	pyrrolidinyl
CH=CHCH <sub>2</sub> CH <sub>3</sub>	Hex	piperidinyl
CH=CHCH <sub>2</sub> CF <sub>3</sub>	Et	Ph
CH=CCl <sub>2</sub>	<i>i</i> -Pr	PhO
OCH <sub>2</sub> CH=CH <sub>2</sub>	<i>c</i> -Pr	4-Me-Ph
CH <sub>2</sub> CH <sub>2</sub> OMe	<i>c</i> -Hex	3-CF <sub>3</sub> -Ph
OCHF <sub>2</sub>	2-Me- <i>c</i> -Pr	4- <i>i</i> -Pr-PhO
C≡CH	CF <sub>3</sub>	4-F <sub>2</sub> HCO-Ph
C≡CCH <sub>2</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	3-Et-PhO
OCH <sub>2</sub> C≡CH	SMe	4-MeO-PhO
NH <sub>2</sub>	SBu	4-MeO-Ph
NMe <sub>2</sub>	S(O)Me	
NH <sub>2</sub> Et	S(O)Bu	

$G^2=S$ ,  $R^9=R^{10}=Me$ ,

 $X=CH$ ,  $Y=CR^{14}$ 
 $R^{14}$ 

Cl

Br

F

Me

Et

OMe

OEt

H

 $G^2=O$ ,  $Y=N$ ,  $X=CH$ ,

 $R^{10}=H$ 
 $R^9$ 

H

Cl

Br

F

CN

OH

Me

Hex

Et

i-Pr

c-Pr

c-Hex

2-Me-c-Pr

CF<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>

SMe

SBu

S(O)Me

S(O)Bu

S(O)<sub>2</sub>MeS(O)<sub>2</sub>Bu

OMe

OBu

OCH<sub>2</sub>CF<sub>3</sub>O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>CH<sub>2</sub>OMe(CH<sub>2</sub>)<sub>3</sub>OMe

CH=CHMe

CH=CHCH<sub>2</sub>CH<sub>3</sub>CH=CHCH<sub>2</sub>CF<sub>3</sub>CH=CCl<sub>2</sub>OCH<sub>2</sub>CH=CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OMeOCHF<sub>2</sub>

C≡CH

C≡CCH<sub>2</sub>CH<sub>3</sub>OCH<sub>2</sub>C≡CHNH<sub>2</sub>NMe<sub>2</sub>

NEt

4-morpholinyl

pyrrolidinyl

piperidinyl

Ph

PhO

4-Me-Ph

3-CF<sub>3</sub>-Ph

4-i-Pr-PhO

4-F<sub>2</sub>HCO-Ph

3-Et-PhO

4-MeO-PhO

4-MeO-Ph

 $G^2=O$ ,  $R^9=R^{10}=Me$ ,

 $X=CR^{13}$ ,  $Y=N$ 
 $R^{13}$ 

H

Cl

Br

F

CN

OH

Me

Hex

Et

i-Pr

c-Pr

c-Hex

2-Me-c-Pr

CF<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>

SMe

SBu

S(O)Me

S(O)Bu

S(O)<sub>2</sub>MeS(O)<sub>2</sub>Bu

OMe

OBu

OCH<sub>2</sub>CF<sub>3</sub>O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>CH<sub>2</sub>OMe(CH<sub>2</sub>)<sub>3</sub>OMe

CH=CHMe

CH=CHCH<sub>2</sub>CH<sub>3</sub>CH=CHCH<sub>2</sub>CF<sub>3</sub>CH=CCl<sub>2</sub>OCH<sub>2</sub>CH=CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OMeOCHF<sub>2</sub>

C=CH	F	c-Pr
C=CCH <sub>2</sub> CH <sub>3</sub>	CN	CF <sub>3</sub>
OCH <sub>2</sub> C=CH	OH	SMe
NH <sub>2</sub>	Me	S(O)Me
NMe <sub>2</sub>	Et	S(O) <sub>2</sub> Me
NHET	i-Pr	OMe
4-morpholinyl	c-Pr	OEt
pyrrolidinyl	CF <sub>3</sub>	OCH <sub>2</sub> OMe
piperidinyl	SMe	OCH <sub>2</sub> CF <sub>3</sub>
Ph	S(O)Me	C=CHMe
PhO	S(O) <sub>2</sub> Me	C=CMMe
4-Me-Ph	OMe	NMe <sub>2</sub>
3-CF <sub>3</sub> -Ph	OEt	Ph
4-i-Pr-PhO	OCH <sub>2</sub> OMe	PhO
4-F <sub>2</sub> HCO-Ph	OCH <sub>2</sub> CF <sub>3</sub>	4-Me-Ph
3-Et-PhO	C=CHMe	4-MeO-Ph
4-MeO-PhO	C=CMMe	H
4-MeO-Ph	NMe <sub>2</sub>	G <sup>2</sup> =O, R <sup>9</sup> =Me, X=Y=N
G <sup>2</sup> =O, R <sup>9</sup> =R <sup>10</sup> =Me,	Ph	R <sup>10</sup>
X=CH, Y=CR <sup>14</sup>	PhO	Cl
R <sup>14</sup>	4-Me-Ph	Br
Cl	4-MeO-Ph	F
Br	H	CN
F	G <sup>2</sup> =S, R <sup>9</sup> =Me, Y=CH,	OH
Me	X=N	Me
Et	R <sup>10</sup>	Et
OMe	Cl	i-Pr
OEt	Br	c-Pr
H	F	CF <sub>3</sub>
G <sup>2</sup> =S, R <sup>9</sup> =Me, X=Y=N	CN	SMe
R <sup>10</sup>	OH	S(O)Me
Cl	Me	S(O) <sub>2</sub> Me
Br	Et	OMe
	i-Pr	OEt



OCH<sub>2</sub>OMeOCH<sub>2</sub>CF<sub>3</sub>

C=CHMe

C=CMc

NMe<sub>2</sub>

Ph

PhO

4-Me-Ph

4-MeO-Ph

H

G<sup>2</sup>=O, R<sup>9</sup>=Me, Y=CH,

X=N

R<sup>10</sup>

Cl

Br

F

CN

OH

Me

Et

i-Pr

c-Pr

CF<sub>3</sub>

SMe

S(O)Me

S(O)<sub>2</sub>Me

OMe

OEt

OCH<sub>2</sub>OMeOCH<sub>2</sub>CF<sub>3</sub>

C=CHMe

C=CMc

NMe<sub>2</sub>

Ph

PhO

4-Me-Ph

4-MeO-Ph

H

G<sup>2</sup>-S

X

Y

R<sup>14</sup>R<sup>9</sup>R<sup>13</sup>R<sup>10</sup>

N

CR<sup>14</sup>-(CH<sub>2</sub>)<sub>3</sub>-

--

Me

CH

CR<sup>14</sup>-(CH<sub>2</sub>)<sub>3</sub>-

--

Me

N

CR<sup>14</sup>-(CH<sub>2</sub>)<sub>4</sub>-

--

Me

CH

CR<sup>14</sup>-(CH<sub>2</sub>)<sub>4</sub>-

--

Me

CR<sup>13</sup>

N

--

-(CH<sub>2</sub>)<sub>3</sub>-

--

Me

CR<sup>13</sup>

CH

--

-(CH<sub>2</sub>)<sub>3</sub>-

--

Me

CR<sup>13</sup>

N

--

-(CH<sub>2</sub>)<sub>4</sub>-

--

Me

CR<sup>13</sup>

CH

--

-(CH<sub>2</sub>)<sub>4</sub>-

--

Me

CR<sup>13</sup>

CH

--

Me

-(CH<sub>2</sub>)<sub>3</sub>-CR<sup>13</sup>

CH

--

Me

-(CH<sub>2</sub>)<sub>4</sub>-G<sup>2</sup>=O

X

Y

R<sup>14</sup>R<sup>9</sup>R<sup>13</sup>R<sup>10</sup>

N

CR<sup>14</sup>-(CH<sub>2</sub>)<sub>3</sub>-

--

Me

CH

CR<sup>14</sup>-(CH<sub>2</sub>)<sub>3</sub>-

--

Me

N

CR<sup>14</sup>-(CH<sub>2</sub>)<sub>4</sub>-

--

Me

CH

CR<sup>14</sup>-(CH<sub>2</sub>)<sub>4</sub>-

--

Me

CR<sup>13</sup>

N

--

-(CH<sub>2</sub>)<sub>3</sub>-

Me

CR <sup>13</sup>	CH	--	-(CH <sub>2</sub> ) <sub>3</sub> -	Me
CR <sup>13</sup>	N	--	-(CH <sub>2</sub> ) <sub>4</sub> -	Me
CR <sup>13</sup>	CH	--	-(CH <sub>2</sub> ) <sub>4</sub> -	Me
CR <sup>13</sup>	CH	--	Me	-(CH <sub>2</sub> ) <sub>3</sub> -
CR <sup>13</sup>	CH	--	Me	-(CH <sub>2</sub> ) <sub>4</sub> -

TABLE 12

Compounds of Formula IID

G<sup>2</sup>=S, X=Y=N, R<sup>11</sup>=R<sup>12</sup>=R<sup>28</sup>=H

R <sup>10</sup>	<i>c</i> -Pr	C=CHMe
Cl	CF <sub>3</sub>	C=CHMe
Br	SMe	NMe <sub>2</sub>
F	S(O)Me	Ph
CN	S(O) <sub>2</sub> Me	PhO
OH	OMe	4-Me-Ph
Me	OEt	4-MeO-Ph
Et	OCH <sub>2</sub> OMe	H
<i>i</i> -Pr	OCH <sub>2</sub> CF <sub>3</sub>	

G<sup>2</sup>=S, R<sup>10</sup>=Me

X	Y	R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>	R <sup>31</sup>
CH	N	H	H	H	H
N	CH	H	H	H	H
N	N	H	3-Me	4-Me	H
N	N	H	3-Me	4-Me	6-Me
N	N	Me	H	H	7-Me
N	N	H	H	4- <i>i</i> -Pr	6-OMe
N	N	H	3-Me	H	7-CF <sub>3</sub>
N	N	H	H	4-Et	7-Et
N	N	H	H	4- <i>i</i> -Pr	6-OCHF <sub>2</sub>
N	N	H	H	H	8-Bu
N	N	H	H	4- <i>c</i> -Pr	6-OEt

$G^2=O$ ,  $X=Y=N$ ,  $R^{11}=R^{12}=R^{28}=H$ 

$R^{10}$	$C-Pr$	$OCH_2CF_3$
Cl	$CF_3$	$C=CHMe$
Br	$SMe$	$C=CMe$
F	$S(O)Me$	$NMe_2$
CN	$S(O)_2Me$	Ph
OH	OMe	PhO
Me	OEt	4-Me-Ph
Et	$OCH_2OMe$	4-MeO-Ph
i-Pr		H

 $G^2=O$ ,  $R^{10}=Me$ 

X	Y	$R^{11}$	$R^{12}$	$R^{28}$	$R^{31}$
CH	N	H	H	H	H
N	CH	H	H	H	H
N	N	H	3-Me	4-Me	H
N	N	H	3-Me	4-Me	6-Me
N	N	Me	H	H	7-Me
N	N	H	H	4-i-Pr	6-OMe
N	N	H	3-Me	H	7- $CF_3$
N	N	H	H	4-Et	7-Et
N	N	H	H	4-i-Pr	6- $OCHF_2$
N	N	H	H	H	8-Bu
N	N	H	H	4-C-Pr	6-OEt

TABLE 13

## Compounds of Formula IIe

$G^2=S$ , $R^{12}=H$ , $R^{28}=H$		$G^2=S$ , $R^{11}=H$ , $R^{28}=H$
$R^{11}$	Br	$R^{12}$
H	$CF_3$	3-Me
Me	OMe	3-Et
Et	OEt	3-i-Pr
i-Pr	$OCHF_2$	3-s-Bu
s-Bu	OBu	3-F
F	$O(CH_2)_3CF_3$	3-Cl
Cl	$(CH_2)_3CF_3$	3-Br

3-CF<sub>3</sub>  
 3-OMe  
 3-OEt  
 3-OCHF<sub>2</sub>  
 3-OBu  
 3-O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 3-(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
  
 G<sup>2</sup>=S, R<sup>11</sup>=R<sup>12</sup>=H  
 R<sup>28</sup>  
 4-Me  
 4-CN  
 4-NO<sub>2</sub>  
 4-OH  
 4-CO<sub>2</sub>H  
 4-CO<sub>2</sub>Et  
 4-Et  
 4-*i*-Pr  
 4-*n*-Hex  
 4-*c*-Pr  
 4-CF<sub>3</sub>  
 4-SMe  
 4-SBu  
 4-*c*-Hex  
 4-Cl  
 4-Br  
 4-F  
 4-(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 4-S(O)Me  
 4-S(O)Bu  
 4-S(O)<sub>2</sub>Me  
 4-S(O)<sub>2</sub>Bu  
 4-OMe  
 4-OBu  
 4-OCH<sub>2</sub>CF<sub>3</sub>

4-OCH<sub>2</sub>OMe  
 4-CH<sub>2</sub>OMe  
 4-CH=CH-Me  
 4-CH=CHCH<sub>2</sub>Me  
 4-TBS  
 4-SiMe<sub>3</sub>  
 4-C≡CH  
 4-C≡C-Et  
 4-OCH<sub>2</sub>C≡CH  
 4-NMe<sub>2</sub>  
 4-C(=O)NMe<sub>2</sub>  
 4-Ph  
 4-OPh  
 4-SPh  
 4-(3-Me-Ph)  
  
 G<sup>2</sup>=S  
 R<sup>11</sup>   R<sup>12</sup>   R<sup>28</sup>  
 Cl   H   6-Cl  
 H   3-Me   4-Me  
 H   3-Me   4-Et  
 H   3-OMe   4-OMe  
 Me   H   5-Me  
 Me   H   4-Me  
 Me   4-Me   5-Me  
 H   3-Cl   5-Cl  
 Cl   H   4-Cl  
  
 G<sup>2</sup>=O, R<sup>12</sup>=H, R<sup>28</sup>=H  
 R<sup>11</sup>  
 H  
 Me  
 Et  
*i*-Pr  
*s*-Bu

F  
 Cl  
 Br  
 CF<sub>3</sub>  
 OMe  
 OEt  
 OCHF<sub>2</sub>  
 OBu  
 O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 (CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
  
 G<sup>2</sup>=O, R<sup>11</sup>=H, R<sup>28</sup>=H  
 R<sup>12</sup>  
 3-Me  
 3-Et  
 3-*i*-Pr  
 3-*s*-Bu  
 3-F  
 3-Cl  
 3-Br  
 3-CF<sub>3</sub>  
 3-OMe  
 3-OEt  
 3-OCHF<sub>2</sub>  
 3-OBu  
 3-O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 3-(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 4-Me  
  
 G<sup>2</sup>=O, R<sup>11</sup>=R<sup>12</sup>=H  
 R<sup>28</sup>  
 4-CN  
 4-NO<sub>2</sub>  
 4-OH  
 4-CO<sub>2</sub>H

4-CO<sub>2</sub>Et  
 4-Et  
 4-*i*-Pr  
 4-*n*-Hex  
 4-*c*-Pr  
 4-CF<sub>3</sub>  
 4-SMe  
 4-SBu  
 4-*c*-Hex  
 4-Cl  
 4-Br  
 4-F  
 4-(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 4-S(O)Me  
 4-S(O)Bu  
 4-S(O)<sub>2</sub>Me  
 4-S(O)<sub>2</sub>Bu  
 4-OMe  
 4-OBu  
 4-OCH<sub>2</sub>CF<sub>3</sub>  
 4-OCH<sub>2</sub>OMe  
 4-CH<sub>2</sub>OMe  
 4-CH=CH-Me  
 4-CH=CHCH<sub>2</sub>Me  
 4-TBS  
 4-SiMe<sub>3</sub>  
 4-C≡CH  
 4-C≡C-Et  
 4-OCH<sub>2</sub>C≡CH  
 4-NMe<sub>2</sub>  
 4-C(=O)NMe<sub>2</sub>  
 4-Ph  
 4-OPh  
 4-SPh  
 4-(3-Me-Ph)

G<sup>2</sup>=O  
 R<sup>11</sup> R<sup>12</sup> R<sup>28</sup>  
 Cl H 6-Cl  
 H 3-Me 4-Me  
 H 3-Me 4-Et  
 H 3-OMe 4-OMe  
 Me H 5-Me  
 Me H 4-Me  
 Me 4-Me 5-Me  
 H 3-Cl 5-Cl  
 Cl H 4-Cl

G<sup>2</sup>=S(O), R<sup>12</sup>=H,  
 R<sup>28</sup>=H

R<sup>11</sup>  
 H  
 Me  
 Et  
*i*-Pr  
*s*-Bu  
 F  
 Cl  
 Br  
 CF<sub>3</sub>  
 OMe  
 OEt  
 OCHF<sub>2</sub>  
 OBu  
 O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 (CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>

G<sup>2</sup>=S(O), R<sup>11</sup>=H,

R<sup>28</sup>=H

R<sup>12</sup>

3-Me

3-Et

3-*i*-Pr

3-*s*-Bu

3-F

3-Cl

3-Br

3-CF<sub>3</sub>

3-OMe

3-OEt

3-OCHF<sub>2</sub>

3-OBu

3-O(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>

3-(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>

G<sup>2</sup>=S(O), R<sup>11</sup>=R<sup>12</sup>=H

R<sup>28</sup>

4-Me

4-CN

4-NO<sub>2</sub>

4-OH

4-CO<sub>2</sub>H

4-CO<sub>2</sub>Et

4-Et

4-*i*-Pr

4-*n*-Hex

4-*c*-Pr

4-CF<sub>3</sub>

4-SMe

4-SBu

4-*c*-Hex

4-Cl

4-Br	H	3-Cl	5-Cl	3-OCHF <sub>2</sub>
4-F	Cl	H	4-Cl	3-OBu
4-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	G <sup>2</sup> =S(O) <sub>2</sub> , R <sup>12</sup> =H,			3-O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
4-S(O)Me	R <sup>28</sup> =H			3-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
4-S(O)Bu	R <sup>11</sup>			G <sup>2</sup> =S(O) <sub>2</sub> ,
4-S(O) <sub>2</sub> Me	H			R <sup>11</sup> -R <sup>12</sup> =H
4-S(O) <sub>2</sub> Bu	Me			R <sup>28</sup>
4-OMe	Et			4-Me
4-OBu	i-Pr			4-CN
4-OCH <sub>2</sub> CF <sub>3</sub>	s-Bu			4-NO <sub>2</sub>
4-OCH <sub>2</sub> OMe	F			4-OH
4-CH <sub>2</sub> OMe	Cl			4-CO <sub>2</sub> H
4-CH=CH-Me	Br			4-CO <sub>2</sub> Et
4-CH=CHCH <sub>2</sub> Me	CF <sub>3</sub>			4-Et
4-TBS	OMe			4-i-Pr
4-SiMe <sub>3</sub>	OEt			4-n-Hex
4-C≡CH	OCHF <sub>2</sub>			4-c-Pr
4-C≡C-Et	OBu			4-CF <sub>3</sub>
4-OCH <sub>2</sub> C≡CH	O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>			4-SMe
4-NMe <sub>2</sub>	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>			4-SBu
4-C(=O)NMe <sub>2</sub>	G <sup>2</sup> =S(O) <sub>2</sub> , R <sup>11</sup> =H,			4-c-Hex
4-Ph	R <sup>28</sup> =H			4-Cl
4-OPh	R <sup>12</sup>			4-Br
4-SPh	3-Me			4-F
4-(3-Me-Ph)	3-Et			4-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
G <sup>2</sup> =S(O)	3-i-Pr			4-S(O)Me
R <sup>11</sup> R <sup>12</sup> R <sup>28</sup>	3-s-Bu			4-S(O)Bu
Cl H 6-Cl	3-F			4-S(O) <sub>2</sub> Me
H 3-Me 4-Me	3-Cl			4-S(O) <sub>2</sub> Bu
H 3-Me 4-Et	3-Br			4-OMe
H 3-OMe 4-OMe	3-CF <sub>3</sub>			4-OBu
Me H 5-Me	3-OMe			4-OCH <sub>2</sub> CF <sub>3</sub>
Me H 4-Me	3-OEt			4-OCH <sub>2</sub> OMe
Me 4-Me 5-Me				4-CH <sub>2</sub> OMe

4-CH=CH-Me  
 4-CH=CHCH<sub>2</sub>Me  
 4-TBS  
 4-SiMe<sub>3</sub>  
 4-C≡CH  
 4-C≡C-Et  
 4-OCH<sub>2</sub>C≡CH  
 4-NMe<sub>2</sub>  
 4-C(=O)NMe<sub>2</sub>  
 4-Ph  
 4-OPh  
 4-SPh  
 4-(3-Me-Ph)

G<sup>2</sup>=S(O)<sub>2</sub>  

R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>
Cl	H	6-Cl
H	3-Me	4-Me
H	3-Me	4-Et
H	3-OMe	4-OMe
Me	H	5-Me
Me	H	4-Me
Me	4-Me	5-Me
H	3-Cl	5-Cl
Cl	H	4-Cl

TABLE 14

Compounds of  
 Formula IIf

n<sup>1</sup>=1  
 R<sup>27</sup>  
 H  
 Et  
 Bu  
 i-Pr

CHF<sub>2</sub>  
 (CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 CO<sub>2</sub>Et  
 C(=O)Me  
 C(=O)(CH<sub>2</sub>)<sub>3</sub>Me  
 C(=O)Ph  
 (3-Me-Ph)C(=O)  
 (4-OMe-Ph)C(=O)  
 CH<sub>2</sub>C=CH<sub>2</sub>  
 CH<sub>2</sub>C≡CH  
 PhCH<sub>2</sub>  
 4-Me-PhCH<sub>2</sub>  
 S(O)<sub>2</sub>Me  
 C(=O)NMe<sub>2</sub>  
 C(=S)NHMe  
 S(O)Me  
 S(O)<sub>2</sub>Ph  
 (4-Me-Ph)S(O)<sub>2</sub>  
 C(=O)NHPh  
 C(=S)NHPh  
 P(=S)(OEt)<sub>2</sub>  
 P(=O)(OEt)<sub>2</sub>  
 S(O)<sub>2</sub>N(Et)<sub>2</sub>  
 n<sup>1</sup>=2  
 R<sup>27</sup>  
 H  
 Et  
 Bu  
 i-Pr  
 CHF<sub>2</sub>  
 (CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 CO<sub>2</sub>Et  
 C(=O)Me  
 C(=O)(CH<sub>2</sub>)<sub>3</sub>Me  
 C(=O)Ph  
 (3-Me-Ph)C(=O)  
 (3-Me-Ph)C(=O)  
 CH<sub>2</sub>C=CH<sub>2</sub>  
 CH<sub>2</sub>C≡CH

C(=O)Ph  
 (3-Me-Ph)C(=O)  
 (4-OMe-Ph)C(=O)  
 CH<sub>2</sub>C=CH<sub>2</sub>  
 CH<sub>2</sub>C≡CH  
 PhCH<sub>2</sub>  
 4-Me-PhCH<sub>2</sub>  
 S(O)<sub>2</sub>Me  
 C(=O)NMe<sub>2</sub>  
 C(=S)NHMe  
 S(O)Me  
 S(O)<sub>2</sub>Ph  
 (4-Me-Ph)S(O)<sub>2</sub>  
 C(=O)NHPh  
 C(=S)NHPh  
 P(=S)(OEt)<sub>2</sub>  
 P(=O)(OEt)<sub>2</sub>  
 S(O)<sub>2</sub>N(Et)<sub>2</sub>  
 n<sup>1</sup>=3  
 R<sup>27</sup>  
 H  
 Et  
 Bu  
 i-Pr  
 CHF<sub>2</sub>  
 (CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>  
 CO<sub>2</sub>Et  
 C(=O)Me  
 C(=O)(CH<sub>2</sub>)<sub>3</sub>Me  
 C(=O)Ph  
 (3-Me-Ph)C(=O)  
 (3-Me-Ph)C(=O)  
 CH<sub>2</sub>C=CH<sub>2</sub>  
 CH<sub>2</sub>C≡CH

PhCH<sub>2</sub>  
 4-Me-PhCH<sub>2</sub>  
 S(O)<sub>2</sub>Me  
 C(=O)NMe<sub>2</sub>  
 C(=S)NHMe  
 S(O)Me  
 S(O)<sub>2</sub>Ph  
 (4-Me-Ph)S(O)<sub>2</sub>  
 C(=O)NHPH  
 C(=S)NHPH  
 P(=S)(OEt)<sub>2</sub>  
 P(=O)(OEt)<sub>2</sub>  
 S(O)<sub>2</sub>N(Et)<sub>2</sub>

TABLE 15  
 Compounds of  
 Formula IIg

n	n <sup>1</sup>	G <sup>2</sup>
1	1	S
1	2	S
2	1	S
0	3	S
1	1	O
1	2	O
2	1	O
0	3	O

1	1	S(O)
1	2	S(O)
2	1	S(O)
0	3	S(O)
1	1	S(O) <sub>2</sub>
1	2	S(O) <sub>2</sub>
2	1	S(O) <sub>2</sub>
0	3	S(O) <sub>2</sub>
1	1	N-Me
1	2	N-Me
2	1	N-Me

TABLE 16

Compounds of Formula IIh

G<sup>2</sup>=S

n <sup>2</sup>	R <sup>1</sup>	R <sup>7</sup>	R <sup>4</sup>	R <sup>8</sup>
1	Me	H	H	H
1	Bu	H	H	H
1	Me	Me	H	H
1	H	H	Me	H
1	H	H	Bu	H
1	Ph	H	H	H
1	4-Me-Ph	H	H	H
1	4-OMe-Ph	H	H	H
0	Me	H	--	--
0	Bu	H	--	--
0	Me	Me	--	--
0	Ph	H	--	--
0	4-Me-Ph	H	--	--

G<sup>2</sup>=O

n <sup>2</sup>	R <sup>1</sup>	R <sup>7</sup>	R <sup>4</sup>	R <sup>8</sup>
1	Me	H	H	H
1	Bu	H	H	H

1	Me	Me	H	H
1	H	H	Me	H
1	H	H	Bu	H
1	Ph	H	H	H
1	4-Me-Ph	H	H	H
1	4-OMe-Ph	H	H	H
0	Me	H	--	--
0	Bu	H	--	--
0	Me	Me	--	--
0	Ph	H	--	--
0	4-Me-Ph	H	--	--

TABLE 17

Compounds of Formula IIi

G<sup>2</sup>=S

n <sup>2</sup>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
0	Me	H	--
0	Bu	H	--
0	H	Me	--
0	H	Bu	--
0	Ph	H	--
0	4-Me-Ph	H	--



0	H	4-OMe-Ph	--
n	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
1	Me	H	H
1	Bu	H	H
1	H	Me	H
1	H	Bu	H
1	H	H	Me
1	H	H	Bu
1	Ph	H	H
1	4-Me-Ph	H	H
1	H	Ph	H
1	H	4-Me-Ph	H
1	H	H	Ph
1	H	H	4-Me-Ph
G <sup>2</sup> =O			
n	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
0	Me	H	--
0	Bu	H	--

0	H	Me	--
0	H	Bu	--
0	Ph	H	--
0	4-Me-Ph	H	--
0	H	4-OMe-Ph	--
1	Me	H	H
1	Bu	H	H
1	H	Me	H
1	H	Bu	H
1	H	H	Me
1	H	H	Bu
1	Ph	H	H
1	4-Me-Ph	H	H
1	H	Ph	H
1	H	4-Me-Ph	H
1	H	H	Ph
1	H	H	4-Me-Ph

TABLE 18

Compounds of Formula IIj

G <sup>2</sup> =S				H	H	H	4-OMe-Ph
R <sup>1</sup>	R <sup>7</sup>	R <sup>5</sup>	R <sup>6</sup>	Bu	H	H	H
H	H	Me	H	3-Me-Ph	H	H	H
H	H	Ph	H	4-OMe-Ph	H	H	H
H	H	H	Me	G <sup>2</sup> =O			
H	H	H	Ph	R <sup>1</sup>	R <sup>7</sup>	R <sup>5</sup>	R <sup>6</sup>
Me	H	H	H	H	H	Me	H
Me	Me	H	H	H	H	Ph	H
Ph	H	H	H	H	H	H	Me
H	Ph	H	H	H	H	H	Ph
H	H	Bu	H	Me	H	H	H
H	H	4-Me-Ph	H	Me	Me	H	H
H	H	H	Bu	Ph	H	H	H

H	Ph	H	H
H	H	Bu	H
H	H	4-Me-Ph	H
H	H	H	Bu
H	H	H	4-OMe-Ph
Bu	H	H	H
3-Me-Ph	H	H	H
4-OMe-Ph	H	H	H

TABLE 19

Compounds of Formula IVc

G <sup>2</sup>	n	n <sup>1</sup>
S	1	1
S	1	2
S	2	1
O	1	1
O	1	2
O	2	1
S(O)	1	1
S(O)	1	2
S(O)	2	1
S(O) <sub>2</sub>	1	1
S(O) <sub>2</sub>	1	2
S(O) <sub>2</sub>	2	1
NMe	1	1
NMe	1	2
NMe	2	1

TABLE 20

Compounds of Formula Im

G<sub>2</sub>=S, MCl<sub>x</sub>=ZnCl<sub>2</sub>

R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>
H	Me	H
H	Et	H
H	OMe	H

H	i-Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H
3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

G<sub>2</sub>=O, MCl<sub>x</sub>=ZnCl<sub>2</sub>

R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>
H	Me	H
H	Et	H
H	OMe	H
H	i-Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H
3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

G<sub>2</sub>=S, MCl<sub>x</sub>=FeCl<sub>3</sub>

R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>
H	Me	H
H	Et	H
H	OMe	H
H	i-Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H
3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

$G_2=O$ , $MCl_x=FeCl_3$		
$R^{11}$	$R^{12}$	$R^{28}$
H	Me	H
H	Et	H
H	OMe	H
H	<i>i</i> -Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H
3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

$G_2=S$ , $MCl_x=CuCl_2$		
$R^{11}$	$R^{12}$	$R^{28}$
H	Me	H
H	Et	H
H	OMe	H
H	<i>i</i> -Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H
3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

$G_2=O$ , $MCl_x=CuCl_2$		
$R^{11}$	$R^{12}$	$R^{28}$
H	Me	H
H	Et	H
H	OMe	H
H	<i>i</i> -Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H

3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

$G_2=S$ , $MCl_x=MnCl_2$		
$R^{11}$	$R^{12}$	$R^{28}$
H	Me	H
H	Et	H
H	OMe	H
H	<i>i</i> -Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H
3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

$G_2=O$ , $MCl_x=MnCl_2$		
$R^{11}$	$R^{12}$	$R^{28}$
H	Me	H
H	Et	H
H	OMe	H
H	<i>i</i> -Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H
3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

$G_2=S$ , $MCl_x=MgCl_2$		
$R^{11}$	$R^{12}$	$R^{28}$
H	Me	H
H	Et	H
H	OMe	H

H	<i>i</i> -Pr	H	H	Et	H
2-Cl	H	H	H	OMe	H
3-Cl	H	H	H	<i>i</i> -Pr	H
H	Cl	H	2-Cl	H	H
3-Me	Me	H	3-Cl	H	H
2-Me	H	5-Me	H	Cl	H
2-Cl	H	6-Cl	3-Me	Me	H
			2-Me	H	5-Me
			2-Cl	H	6-Cl
$G_2=O, MCl_x=MeCl_2$					
R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>			
H	Me	H			

Formulation/Utility

Compounds of this invention will generally be used in formulation with an agriculturally suitable composition. The fungicidal compositions of the present invention comprise an effective amount of at least one compound of Formula I as defined above and at least one of (a) a surfactant, (b) an organic solvent, and (c) at least one solid or liquid diluent. Useful formulations can be prepared in conventional ways. They include dusts, granules, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates, dry flowables and the like. Sprayable formulations can be extended in suitable media and used at spray volumes from about one to several hundred liters per hectare. High strength compositions are primarily used as intermediates for further formulation. The formulations will typically contain effective amounts of active ingredient, diluent and surfactant within the following approximate ranges which add up 100 weight percent.

	Weight Percent		
	Active Ingredient	Diluent	Surfactant
Wettable Powders	25-90	0-74	1-10
Oil Suspensions, Emulsions, Solutions, (including Emulsifiable Concentrates)	5-50	40-95	0-15
Dusts	1-25	70-99	0-5
Granules, Baits and Pellets	0.01-99	5-99.99	0-15
High Strength Compositions	90-99	0-10	0-2

Typical solid diluents are described in Watkins, et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey.

- 5 Typical liquid diluents and solvents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950. *McCutcheon's Detergents and Emulsifiers Annual*, Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, *Encyclopedia of Surface Active*
- 10 *Agents*, Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth, etc.

- 15 Methods for formulating such compositions are well known. Solutions are prepared by simply mixing the ingredients. Fine solid compositions are made by blending and, usually, grinding as in a hammer mill or fluid energy mill. Water-dispersible granules can be produced by agglomerating a fine powder composition;
- 20 see for example, Cross et al., *Pesticide Formulations*, Washington, D.C., 1988, pp 251-259. Suspensions are prepared by wet-milling; see, for example, U.S. 3,060,084. Granules and pellets can be made by

spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", *Chemical Engineering*, December 4, 1967, pp 147-148, *Perry's Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill, New York, 1963, pp 8-57 and following, and WO 91/13546. Pellets can be prepared as described in U.S. 4,172,714. Water-dispersible and water-soluble granules can be prepared as taught in DE 3,246,493.

10 For further information regarding the art of formulation, see U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10 through 41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 15 138-140, 162-164, 166, 167 and 169-182; U.S. 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1-4; Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, 1961, pp 81-96; and Hance et al., *Weed Control Handbook*, 8th Ed., Blackwell 20 Scientific Publications, Oxford, 1989.

In the following Examples, all percentages are by weight and all formulations are worked up in conventional ways. Compound numbers refer to Index Table A hereinafter.

25 Example A

Wettable Powder

Compound 11	65.0%
dodecylphenol polyethylene glycol ether	2.0%
sodium ligninsulfonate	4.0%
30 sodium silicoaluminate	6.0%
montmorillonite (calcined)	23.0%.

Example B

Granule

Compound 11	10.0%
35 attapulgate granules (low volative	

matter, 0.71/0.30 mm; U.S.S. No.  
25-50 sieves) 90.0%.

Example CExtruded Pellet

5	Compound 11	25.0%
	anhydrous sodium sulfate	10.0%
	crude calcium ligninsulfonate	5.0%
	sodium alkyl naphthalenesulfonate	1.0%
	calcium/magnesium bentonite	59.0%.

10 Example DEmulsifiable Concentrate

	Compound 11	20.0%
	blend of oil soluble sulfonates and polyoxyethylene ethers	10.0%
15	isophorone	70.0%.

The compounds of this invention are useful as plant disease control agents. The present invention therefore further comprises a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected, an effective amount of a compound of Formula I or a fungicidal composition containing said compound. The compounds and compositions of this invention provide control of diseases caused by a broad spectrum of fungal plant pathogens in the *Basidiomycete*, *Ascomycete*, *Oomycete* and *Deuteromycete* classes. They are effective in controlling a broad spectrum of plant diseases, particularly foliar pathogens of ornamental, vegetable, field, cereal, and fruit crops. These pathogens include *Plasmopara viticola*, *Phytophthora infestans*, *Peronospora tabacina*, *Pseudoperonospora cubensis*, *Pythium aphanidermatum*, *Alternaria brassicae*, *Septoria nodorum*, *Cercosporidium personatum*, *Cercospora arachidicola*, *Pseudocercospora herpotrichoides*,

*Cercospora beticola*, *Botrytis cinerea*, *Monilinia fructicola*, *Pyricularia oryzae*, *Podosphaera leucotricha*, *Venturia inaequalis*, *Erysiphe graminis*, *Uncinula necatur*, *Puccinia recondita*, *Puccinia graminis*, *Hemileia vastatrix*, *Puccinia striiformis*, *Puccinia arachidis*, *Rhizoctonia solani*, *Sphaerotheca fuliginea*, *Fusarium oxysporum*, *Verticillium dahliae*, *Pythium aphanidermatum*, *Phytophthora megasperma* and other genera and species closely related to these pathogens.

Compounds of this invention can also be mixed with one or more other insecticides, fungicides, nematocides, bactericides, acaricides, semiochemicals, repellants, attractants, pheromones, feeding stimulants or other biologically active compounds to form a multi-component pesticide giving an even broader spectrum of agricultural protection. Examples of other agricultural protectants with which compounds of this invention can be formulated are: insecticides such as monocrotophos, carbofuran, tetrachlorvinphos, malathion, parathion-methyl, methomyl, chlordimeform, diazinon, deltamethrin, oxamyl, fenvalerate, esfenvalerate, permethrin, profenofos, sulprofos, triflumuron, diflubenzuron, methoprene, buprofezin, thiodicarb, acephate, azinphosmethyl, chlorpyrifos, dimethoate, fipronil, flufenprox, fonophos, isofenphos, methidathion, methamidophos, phosmet, phosphamidon, phosalone, pirimicarb, phorate, terbufos, trichlorfon, methoxychlor, bifenthrin, biphenate, cyfluthrin, fenpropathrin, fluvalinate, flucythrinate, tralomethrin, metaldehyde and rotenone; fungicides such as carbendazim, thiuram, dodine, maneb, chloroneb, benomyl, cymoxanil, fenpropidine, fenpropimorph, triadimefon, captan, thiophanate-methyl, thiabendazole, phosethyl-Al, chlorothalonil, dichloran, metalaxyl,



- captafol, iprodione, oxadixyl, vinclozolin, kasugamycin, myclobutanil, tebuconazole, difenoconazole, diniconazole, fluquinconazole, ipconazole, metconazole, penconazole, propiconazole, 5 uniconazole, flutriafol, prochloraz, pyrifenox, fenarimol, triadimenol, diclobutrazol, copper oxychloride, furalaxyl, folpet, flusilazol, blasticidin S, diclomezine, edifenphos, isoprothiolane, iprobenfos, mepronil, neo-asozin, pencycuron, 10 probenazole, pyroquilon, tricyclazole, validamycin, and flutolanil; nematocides such as aldoxycarb, fenamiphos and fosthietan; bactericides such as oxytetracycline, streptomycin and tribasic copper sulfate; acaricides such as binapacryl, oxythioquinox, chlorobenzilate, 15 dicofol, dienochlor, cyhexatin, hexythiazox, amitraz, propargite, tebufenpyrad and fenbutatin oxide; and biological agents such as *Bacillus thuringiensis*, baculovirus and avermectin B.

- 20 In certain instances, combinations with other fungicides having a similar spectrum of control but a different mode of action will be particularly advantageous for resistance management.

- Plant disease control is ordinarily accomplished by applying an effective amount of a compound of this 25 invention either pre- or post-infection, to the portion of the plant to be protected such as the roots, stems, foliage, fruit, seeds, tubers or bulbs, or to the media (soil or sand) in which the plants to be protected are growing. The compounds can also be applied to the seed 30 to protect the seed and seedling.

- Rates of application for these compounds can be influenced by many factors of the environment and should be determined under actual use conditions. Foliage can normally be protected when treated at a 35 rate of from less than 1 g/ha to 5,000 g/ha of active

Test compounds were first dissolved in acetone in an amount equal to 3% of the final volume and then suspended at a concentration of 200 ppm in purified water containing 250 ppm of the surfactant Trem® 014 (polyhydric alcohol esters). The resulting test suspensions were then used in the following tests.

The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore dust of *Erysiphe graminis* f. sp. *tritici*, (the causal agent of wheat powdery mildew) and incubated in a growth chamber at 20°C for 7 days, after which disease ratings were made.

The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Puccinia recondita* (the causal agent of wheat leaf rust) and incubated in a saturated atmosphere at 20°C for 24 h, and then moved to a growth chamber at 20°C for 6 days, after which disease ratings were made.

The test suspension was sprayed to the point of run-off on rice seedlings. The following day the seedlings were inoculated with a spore suspension of *Pyricularia oryzae* (the causal agent of rice blast) and incubated in a saturated atmosphere at 27°C for 24 h,

and then moved to a growth chamber at 30°C for 5 days, after which disease ratings were made.

#### TEST D

5 The test suspension was sprayed to the point of run-off on tomato seedlings. The following day the seedlings were inoculated with a spore suspension of *Phytophthora infestans* (the causal agent of potato and tomato late blight) and incubated in a saturated atmosphere at 20°C for 24 h, and then moved to a growth  
10 chamber at 20°C for 5 days, after which disease ratings were made.

#### TEST E

The test suspension was sprayed to the point of run-off on grape seedlings. The following day the  
15 seedlings were inoculated with a spore suspension of *Plasmopara viticola* (the causal agent of grape downy mildew) and incubated in a saturated atmosphere at 20°C for 24 h, moved to a growth chamber at 20°C for 6 days, and then incubated in a saturated atmosphere at 20°C  
20 for 24 h, after which disease ratings were made.

#### TEST F

The test suspension was sprayed to the point of run-off on cucumber seedlings. The following day the seedlings were inoculated with a spore suspension of  
25 *Botrytis cinerea* (the causal agent of gray mold on many crops) and incubated in a saturated atmosphere at 20°C for 48 h, and moved to a growth chamber at 20°C for 5 days, after which disease ratings were made.

30

#### Index Table 1

##### Compounds of Formula I

R<sup>9</sup>=R<sup>10</sup>=Me; X=CH; Y=N

Cmpd. No.	G <sup>1</sup> -G <sup>2</sup> -G <sup>3</sup>	E	mp (°C)
1	CH <sub>2</sub> OCH <sub>2</sub>	Ph	a
2	CH <sub>2</sub> CH <sub>2</sub> S	4-Cl-Ph	a

3	$\text{CH}_2\text{OCH}_2$	4-Et-Ph	a
4	$\text{CH}_2\text{CH}_2\text{O}$	3-Me-Ph	a
5	$\text{CH}_2\text{CH}_2\text{S}$	3-Me-Ph	a
6	$\text{CH}_2\text{CH}_2\text{O}$	2,6-diCl-Ph	a
7	$\text{CH}_2\text{CH}_2\text{S}$	4-Me-Ph	a
8	$\text{CH}_2\text{CH}_2\text{S}$	2-Cl-Ph	146-148
9	$\text{CH}_2\text{CH}_2\text{S}$	3-Cl-Ph	a
10	$\text{CH}_2\text{CH}_2\text{O}$	4-Et-Ph	99-106
11	$\text{CH}_2\text{CH}_2\text{S}$	4-Et-Ph	84-87
12	$\text{CH}_2\text{CH}_2\text{SO}$	2-Cl-Ph	168-170
13	$\text{CH}_2\text{CH}_2\text{S}$	Ph	142-145
14	$\text{CH}_2\text{CH}_2\text{S}$	3-CF <sub>3</sub> -Ph	105-110
15	$\text{CH}_2\text{CH}_2\text{S}$	4-OMe-Ph	111-115
16	$\text{CH}_2\text{CH}_2\text{SO}$	4-Et-Ph	149-164
17	$\text{CH}_2\text{CH}_2\text{SO}_2$	4-Et-Ph	139-141
18	$\text{CH}_2\text{CH}_2\text{S}$	4-t-Bu	114-121
19	$\text{CH}_2\text{CH}_2\text{CH}_2\text{S}$	4-OMe-Ph	119-123
20	$\text{CH}_2\text{CH}_2\text{S}$	OPh	75-85
21	$\text{CH}_2\text{CH}_2\text{CH}_2\text{S}$	4-Et-Ph	97-100
22	$\text{CH}(\text{CH}_3)\text{CH}_2\text{S}$	4-Et-Ph	a
23	$\text{CH}_2\text{CH}_2\text{S}$	2-Me-Ph	86-91
24	$\text{CH}_2\text{CH}_2\text{S}$	OBzl	81-93
25	$\text{CH}_2\text{CH}_2\text{S}$	SPh	a
26	$\text{CH}_2\text{CH}_2\text{S}$	Bzl	a
27	$\text{CH}_2\text{CH}_2\text{CH}_2\text{S}$	Ph	158-160
28	$\text{CH}(\text{CH}_3)\text{CH}_2\text{S}$	Ph	a
29	$\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{S}$	Ph	116-121
30	$\text{CH}_2\text{CH}(\text{Ph})\text{S}$	Ph	196-208
31	$\text{CH}_2\text{CH}_2\text{S}$	Et	a
32	$\text{CH}_2\text{CH}(\text{CO}_2\text{Et})\text{S}$	Ph	124-133
33	$\text{CH}_2\text{CH}(\text{Ph})\text{SO}_2$	Ph	201-206
34	$\text{CH}(\text{CF}_3)\text{CH}_2\text{S}$	Ph	174-181
35	$\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{S}$	Ph	a
36	$\text{CH}_2\text{CH}(\text{CN})\text{S}$	Ph	208-212
37	$\text{CH}(\text{CN})\text{CH}_2\text{S}$	Ph	168-174

38	CH <sub>2</sub> CH <sub>2</sub> S	3,4-diCl-Ph	149-152
39	CH <sub>2</sub> CH <sub>2</sub> S	4-Ph-Ph	151-155
40	CH <sub>2</sub> CH <sub>2</sub> S	3,4-diOMe-Ph	172-174

<sup>a</sup> Oil or gum; <sup>1</sup>H NMR data in Index Table 2.

X=CR<sup>13</sup>; R<sup>9</sup> and R<sup>13</sup> are taken together to form a fused benzene ring; Y=N; R<sup>10</sup>=Me

Cmpd. No.	G <sup>1</sup> -G <sup>2</sup> -G <sup>3</sup>	E	mp (°C)
38	CH <sub>2</sub> CH <sub>2</sub> S	Ph	102-108

5

R<sup>9</sup>=R<sup>10</sup>=ethyl; X=CH; Y=N

Cmpd. No.	G <sup>1</sup> -G <sup>2</sup> -G <sup>3</sup>	E	mp (°C)
39	CH <sub>2</sub> CH <sub>2</sub> S	Ph	oil; <sup>1</sup> H NMR data in Index Table 2.

#### Index Table 2

Cmpd. No.	<sup>1</sup> H NMR Data <sup>a</sup>
1	7.75 (m, 2H), 7.37 (m, 3H), 6.57 (s, 1H), 5.54 (s, 2H), 4.83 (s, 2H), 2.42 (s, 6H).
2	7.83 (d, 2H), 7.35 (d, 2H), 6.56 (s, 1H), 4.47 (t, 2H), 3.36 (t, 2H), 2.43 (s, 6H).
3	7.66 (d, 2H), 7.21 (d, 2H), 6.56 (s, 1H), 5.54 (s, 2H), 4.81 (s, 2H), 2.67 (q, 2H), 2.42 (s, 6H), 1.24 (t, 3H).
4	7.82 (m, 1H), 7.75 (m, 1H), 7.25 (m, 1H), 7.19 (m, 1H), 6.49 (s, 1H), 4.54 (m, 2H), 4.28 (m, 2H), 2.42 (s, 6H), 2.38 (s, 3H).
5	7.7 (m, 2H), 7.2 (m, 2H), 6.54 (s, 1H), 4.45 (m, 2H), 3.35 (m, 2H), 2.42 (s, 6H), 2.39 (s, 3H).
6	7.31 (m, 2H), 7.25 (m, 1H), 6.5 (s, 1H), 4.55 (m, 2H), 4.35 (m, 2H), 2.38 (s, 6H).

7	7.77 (d, 2H), 7.18 (d, 2H), 6.53 (s, 1H), 4.46 (m, 2H), 3.35 (m, 2H), 2.42 (s, 6H), 2.37 (s, 3H).
9	7.90 (m, 1H), 7.75 (m, 1H), 7.3 (m, 2H), 6.57 (s, 1H), 4.47 (m, 2H), 3.36 (m, 2H), 2.43 (s, 6H).
22	7.82 (d, 2H), 7.22 (d, 2H), 6.52 (s, 1H), 5.7 (m, 1H), 3.45 (d, 1H), 3.00 (d, 1H), 2.7 (q, 2H), 2.42 (s, 6H), 1.38 (d, 3H), 1.24 (t, 3H).
25	7.65 (m, 2H), 7.34 (m, 3H), 6.55 (s, 1H), 4.40 (m, 2H), 3.25 (m, 2H), 2.41 (s, 6H).
26	7.37 (d, 2H), 7.32 (t, 2H), 7.25 (d, 1H), 6.51 (s, 1H), 4.32 (m, 2H), 3.89 (s, 2H), 3.19 (m, 2H), 2.41 (s, 6H).
28	7.93 (d, 2H), 7.37 (m, 3H), 6.54 (s, 1H), 5.7 (m, 1H), 3.45 (d, 1H), 3.02 (m, 1H), 2.42 (s, 6H), 1.40 (d, 3H).
31	6.48 (s, 1H), 4.33 (t, 2H), 3.25 (t, 2H), 2.58 (q, 2H), 2.39 (s, 6H), 1.26 (t, 3H).
35	7.85 (d, 2H), 7.37 (m, 3H), 6.52 (s, 1H), 5.50 (m, 1H), 3.38 (d, 1H), 3.20 (d, 1H), 2.41 (s, 6H), 1.80 (m, 2H), 0.99 (t, 3H).
39	7.85 (d, 2H), 7.37 (m, 3H), 6.56 (s, 1H), 4.45 (m, 2H), 3.35 (m, 2H), 2.72 (q, 4H), 1.31 (t, 6H).

<sup>a</sup> <sup>1</sup>H NMR data are in ppm downfield from tetramethylsilane. Coupling are designated (s)-singlet, (d)-doublet, (t)-triplet, (q)-quartet, (m)-multiplet. Samples were dissolved in CDCl<sub>3</sub>.

- 5 Results for Tests A-F are given in Table A. In the table, a rating of 100 indicates 100% disease control and a rating of 0 indicates no disease control (relative to the controls). NT = Not Tested.

Table A

Cmpd No.	Test A	Test B	Test C	Test D	Test E	Test F
1	98	100	65	23	75	65
2	76	93	99	11	91	2
3	86*	84*	72*	59*	44	77
4	73*	64*	73*	36*	0*	32*
5	24*	64*	73*	10*	0*	32*
6	0*	0*	29*	0*	86*	46*
8	0	80	85	3	100	98
9	98	100	99	82	92	98
10	94	100	99	52	85	82
11	99	100	97	52	92	98
12	56	0	0	60	92	0
13	98	96	91	91	100	77
14	98	82	100	73	100	47
15	96	98	97	0	100	98
16	82	0	0	0	13	0
17	61	14	0	NT	14	0
18	82	0	86	0	73	83
19	29	21	57	18	96	99
20	90	98	99	85	99	99
21	98	98	94	0	100	69
22	0	55	91	58	100	0
23	74	100	94	73	100	80
24	83	91	32	63	84	0
25	90	100	91	63	100	70
26	92	98	85	70	100	46
27	55	23	91	14	74	98
28	56*	96	91	0	100	94
29	52	80	74	22*	92	94
30	0	55	0	22	99	66
31	89	55	0	44	0	66
32	0	0	0	0	99	82
33	0*	54*	0*	0*	9*	34*
34	0*	54*	0*	0*	0*	0*

82

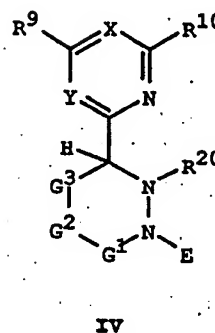
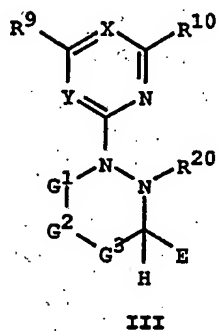
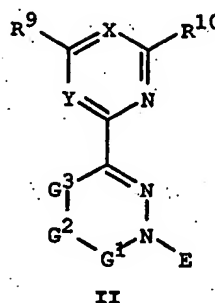
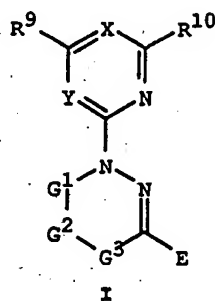
38	29	93	97	23	96	0
39	98	83	91	0	100	90

\*=Applications of the compound was made at a rate of 40 ppm.



What is claimed is:

1. The compounds of Formulae I, II, III and IV,



wherein:

10        -G<sup>1</sup>-G<sup>2</sup>-G<sup>3</sup>- taken together with the attached atoms  
             form a 5-8 membered ring, wherein

             -G<sup>1</sup>- is -CR<sup>1</sup>R<sup>7</sup>-; -(CHR<sup>1</sup>CHR<sup>2</sup>)-; -(CHR<sup>1</sup>CHR<sup>2</sup>CHR<sup>3</sup>)-; or  
             -(CHR<sup>1</sup>CHR<sup>2</sup>CHR<sup>3</sup>CHR<sup>4</sup>)-;

             -G<sup>2</sup>-is -O-; -S-; -S(O)-; -S(O)<sub>2</sub>- or -NR<sup>27</sup>-;

15        -G<sup>3</sup>-is -CR<sup>4</sup>R<sup>8</sup>-; -(CHR<sup>5</sup>CHR<sup>6</sup>)-; -(CHR<sup>3</sup>CHR<sup>5</sup>CHR<sup>6</sup>)- or a  
             direct bond;

             X is N or CR<sup>13</sup>;

             Y is N or CR<sup>14</sup>;

20        E is H; C<sub>1</sub>-C<sub>6</sub> alkyl; C<sub>3</sub>-C<sub>7</sub> cycloalkyl optionally  
             substituted with 1-2 methyl; C<sub>1</sub>-C<sub>6</sub> haloalkyl;  
             C<sub>1</sub>-C<sub>6</sub> alkylthio; C<sub>1</sub>-C<sub>6</sub> alkoxy; C<sub>1</sub>-C<sub>6</sub> haloalkoxy;  
             or phenyl, phenoxy, phenylthio, phenylamino,

phenylmethyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, 2-naphthalenyl, thienyl, furanyl or pyridyl each optionally substituted with R<sup>11</sup>, R<sup>12</sup> and R<sup>28</sup>;

- 5 R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are each independently H; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl, halogen, CO<sub>2</sub>CH<sub>3</sub>, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, cyano or phenyl optionally substituted with R<sup>25</sup>;

provided that

- 10 (i) the maximum number of carbon atoms in -G<sup>1</sup>-G<sup>2</sup>-G<sup>3</sup>- with geminal disubstitution is one;
- (ii) the maximum number of optionally substituted phenyl substituents on
- 15 -G<sup>1</sup>-G<sup>2</sup>-G<sup>3</sup>- is one;
- (iii) -G<sup>3</sup>- is other than a direct bond in compounds of Formulae III and IV; and
- (iv) -G<sup>2</sup>-G<sup>3</sup>- is other than -NR<sup>27</sup>- in compounds of Formulae I and II;

- 20 R<sup>9</sup>, R<sup>10</sup> and R<sup>13</sup> are each independently H; halogen; cyano; hydroxy; C<sub>1</sub>-C<sub>6</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; C<sub>1</sub>-C<sub>4</sub> alkylthio; C<sub>1</sub>-C<sub>4</sub> alkylsulfinyl; C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl; C<sub>3</sub>-C<sub>6</sub> cycloalkyl optionally substituted with 1-2 methyl groups; C<sub>1</sub>-C<sub>4</sub>
- 25 alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy; C<sub>2</sub>-C<sub>4</sub> alkoxyalkyl; C<sub>2</sub>-C<sub>4</sub> alkenyl; C<sub>2</sub>-C<sub>4</sub> haloalkenyl; C<sub>2</sub>-C<sub>4</sub> alkenyloxy; C<sub>2</sub>-C<sub>4</sub> alkynyl; C<sub>2</sub>-C<sub>4</sub> alkynyloxy; NR<sup>29</sup>R<sup>30</sup>; or phenyl or phenoxy optionally substituted with R<sup>31</sup>; or

- 30 R<sup>9</sup> and R<sup>13</sup>, or R<sup>10</sup> and R<sup>13</sup>, or R<sup>9</sup> and R<sup>14</sup> can be taken together to form -(CH<sub>2</sub>)<sub>3</sub>-, -(CH<sub>2</sub>)<sub>4</sub>- or a fused benzene ring optionally substituted with R<sup>31</sup>.

- R<sup>11</sup>, R<sup>12</sup>, R<sup>21</sup>, R<sup>24</sup>, R<sup>26</sup> and R<sup>31</sup> are each independently halogen; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; C<sub>1</sub>-C<sub>4</sub> alkoxy; or C<sub>1</sub>-C<sub>4</sub> haloalkoxy;
- R<sup>14</sup> is H; halogen; C<sub>1</sub>-C<sub>2</sub> alkyl; or C<sub>1</sub>-C<sub>2</sub> alkoxy;
- 5 R<sup>15</sup>, R<sup>16</sup>, R<sup>17</sup>, R<sup>18</sup>, R<sup>29</sup> and R<sup>30</sup> are each independently H or C<sub>1</sub>-C<sub>2</sub> alkyl; or
- R<sup>15</sup> and R<sup>16</sup>, or R<sup>17</sup> and R<sup>18</sup>, or R<sup>29</sup> and R<sup>30</sup> can be taken together along with the nitrogen atom to which they are attached to form a
- 10 4-morpholinyl, pyrrolidinyl or piperidinyl ring;
- R<sup>20</sup> and R<sup>27</sup> are each independently H; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl; phenyl-carbonyl optionally substituted with R<sup>21</sup>; C<sub>3</sub>-C<sub>4</sub> alkenyl; C<sub>3</sub>-C<sub>4</sub> alkynyl; phenylmethyl optionally substituted with R<sup>21</sup> on the phenyl ring; C<sub>1</sub>-C<sub>4</sub> alkylsulfinyl; C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl; phenyl-sulfinyl, phenylsulfonyl or phenoxycarbonyl
- 15 each optionally substituted with R<sup>21</sup>; C<sub>2</sub>-C<sub>4</sub> alkoxy carbonyl; C(=O)NR<sup>22</sup>R<sup>23</sup>; C(=S)NHR<sup>23</sup>; P(=S)(C<sub>1</sub>-C<sub>4</sub> alkoxy)<sub>2</sub>; P(=O)(C<sub>1</sub>-C<sub>4</sub> alkoxy)<sub>2</sub>; or S(=O)<sub>2</sub>NR<sup>22</sup>R<sup>23</sup>;
- R<sup>22</sup> is H or C<sub>1</sub>-C<sub>3</sub> alkyl;
- R<sup>23</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl; or phenyl optionally
- 25 substituted with R<sup>24</sup>; or
- R<sup>22</sup> and R<sup>23</sup> can be taken together along with the nitrogen atom to which they are attached to form a 4-morpholinyl, pyrrolidinyl, piperidinyl or imidazolyl ring;
- 30 R<sup>25</sup> is 1-2 halogen; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy; nitro; cyano or C<sub>1</sub>-C<sub>4</sub> alkylthio; and
- R<sup>28</sup> is halogen; cyano; nitro; hydroxy; hydroxy-carbonyl; C<sub>1</sub>-C<sub>6</sub> alkyl; C<sub>3</sub>-C<sub>6</sub> cycloalkyl; C<sub>1</sub>-C<sub>6</sub> haloalkyl; C<sub>1</sub>-C<sub>4</sub> alkylthio; C<sub>1</sub>-C<sub>4</sub> alkyl-
- 35

sulfinyl; C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl; (C<sub>1</sub>-C<sub>4</sub> alkyl)<sub>3</sub>silyl; C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl; C<sub>2</sub>-C<sub>4</sub> alkenyl; C<sub>3</sub>-C<sub>4</sub> alkenyloxy; C<sub>2</sub>-C<sub>4</sub> alkynyl; C<sub>3</sub>-C<sub>4</sub> alkynyloxy; C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy; C<sub>2</sub>-C<sub>4</sub> alkoxyalkyl; C<sub>2</sub>-C<sub>5</sub> alkoxy carbonyl; C<sub>2</sub>-C<sub>4</sub> alkoxyalkoxy; NR<sup>15</sup>R<sup>16</sup>; C(=O)NR<sup>17</sup>R<sup>18</sup>; or phenyl, phenoxy or phenylthio each optionally substituted with R<sup>26</sup>;

provided that

when E is, C<sub>1</sub>-C<sub>6</sub> alkylthio, C<sub>1</sub>-C<sub>6</sub> alkoxy, C<sub>1</sub>-C<sub>6</sub> haloalkoxy, phenoxy, phenylthio or phenylamino, then E may only substitute compounds of Formula I.

and agriculturally suitable salts and metal complexes thereof.

2. The compounds of Claim 1, Formula I, wherein:

Y is N;

E is phenyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, thienyl, or pyridyl each

optionally substituted with R<sup>11</sup>, R<sup>12</sup> and R<sup>28</sup>;

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are each independently H or methyl;

R<sup>11</sup> and R<sup>12</sup> are each independently F, Cl, methyl, trifluoromethyl, methoxy or trifluoromethoxy;

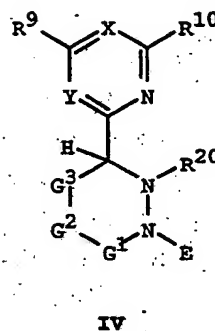
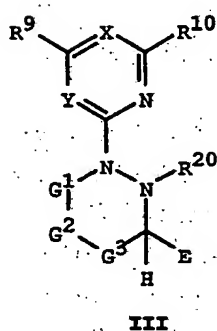
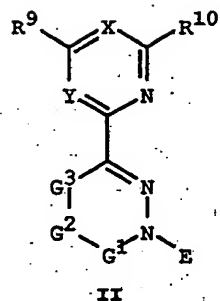
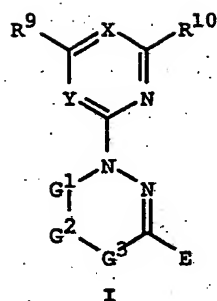
R<sup>13</sup> is H;

R<sup>9</sup> and R<sup>10</sup> are each independently halogen; C<sub>1</sub>-C<sub>4</sub> alkyl; cyclopropyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; allyl; or C<sub>2</sub>-C<sub>3</sub> alkynyl; or

R<sup>9</sup> and R<sup>13</sup> can be taken together to form a fused benzene ring optionally substituted with R<sup>31</sup>;

R<sup>28</sup> is halogen; cyano; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; allyl; propargyl; C<sub>1</sub>-C<sub>4</sub> alkoxy;

- C<sub>1</sub>-C<sub>4</sub> haloalkoxy; or phenyl or phenoxy each optionally substituted with R<sup>26</sup>; and R<sup>31</sup> is halogen; C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> haloalkyl.
3. The compounds of Claim 2, wherein:  
5 G<sup>2</sup> is O; S or NR<sup>27</sup>; and  
E is phenyl optionally substituted with R<sup>11</sup>, R<sup>12</sup> and R<sup>28</sup>; indanyl or tetrahydronaphthalenyl.
4. The compounds of Claim 3, wherein:  
G<sup>2</sup> is O; S; NH or N(C<sub>1</sub>-C<sub>4</sub> alkyl); and  
10 E is phenyl optionally substituted with R<sup>11</sup>, R<sup>12</sup> and R<sup>28</sup>.
5. The compound of Claim 1, which is  
3-(4,6-dimethyl-2-pyrimidinyl)-3,6-dihydro-5-phenyl-2H-1,3,4-oxadiazine.
- 15 6. The compound of Claim 1, which is  
3-(4,6-dimethyl-2-pyrimidinyl)-5-(4-ethyl-phenyl)-3,6-dihydro-2H-1,3,4-oxadiazine.
7. The compound of Claim 1, which is  
2-(2-chlorophenyl)-4-(4,6-dimethyl-2-pyrimidinyl)-5,6-dihydro-4H-1,3,4-thiadiazine.
- 20 8. The compound of Claim 1, which is  
4-(4,6-dimethyl-2-pyrimidinyl)-2-(4-ethyl-phenyl)-5,6-dihydro-4H-1,3,4-thiadiazine.
9. A method of controlling fungus disease in plants  
25 which comprises treating the locus to be protected with an effective amount of at least one of the compounds of Formulae I, II, III or IV, agriculturally suitable salts thereof, agriculturally suitable metal complexes thereof, or agricultural compositions containing them;



5 wherein:

-G<sup>1</sup>-G<sup>2</sup>-G<sup>3</sup>- taken together with the attached atoms form a 5-8 membered ring, wherein

-G<sup>1</sup>- is -CR<sup>1</sup>R<sup>7</sup>-; -(CHR<sup>1</sup>CHR<sup>2</sup>)-; -(CHR<sup>1</sup>CHR<sup>2</sup>CHR<sup>3</sup>)-; or -(CHR<sup>1</sup>CHR<sup>2</sup>CHR<sup>3</sup>CHR<sup>4</sup>)-;

10 -G<sup>2</sup>- is -O-; -S-; -S(O)-; -S(O)<sub>2</sub>- or -NR<sup>27</sup>-;

-G<sup>3</sup>- is -CR<sup>4</sup>R<sup>8</sup>-; -(CHR<sup>5</sup>CHR<sup>6</sup>)-; -(CHR<sup>3</sup>CHR<sup>5</sup>CHR<sup>6</sup>)- or a direct bond;

X is N or CR<sup>13</sup>;

Y is N or CR<sup>14</sup>;

15 E is H; C<sub>1</sub>-C<sub>6</sub> alkyl; C<sub>3</sub>-C<sub>7</sub> cycloalkyl optionally substituted with 1-2 methyl; C<sub>1</sub>-C<sub>6</sub> haloalkyl; C<sub>1</sub>-C<sub>6</sub> alkylthio; C<sub>1</sub>-C<sub>6</sub> alkoxy; C<sub>1</sub>-C<sub>6</sub> haloalkoxy; or phenyl, phenoxy, phenylthio, phenylamino, phenylmethyl, indanyl, tetrahydronaphthalenyl, 20 1-naphthalenyl, 2-naphthalenyl, thienyl, furanyl or pyridyl each optionally substituted with R<sup>11</sup>, R<sup>12</sup> and R<sup>28</sup>;

$R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are each independently H;  $C_1$ - $C_4$  alkyl;  $C_1$ - $C_4$  haloalkyl, halogen,  $CO_2CH_3$ ,  $CO_2CH_2CH_3$ , cyano, or phenyl optionally substituted with  $R^{25}$ ;

5 provided that

(i) the maximum number of carbon atoms in  $-G^1-G^2-G^3-$  with geminal disubstitution is one;

10 (ii) the maximum number of optionally substituted phenyl substituents on  $-G^1-G^2-G^3-$  is one;

(iii)  $-G^3-$  is other than a direct bond in compounds of Formulae III and IV; and

15 (iv)  $-G^2-G^3-$  is other than  $-NR^{27}-$  in compounds of Formulae I and II;

$R^9$ ,  $R^{10}$  and  $R^{13}$  are each independently H; halogen; cyano; hydroxy;  $C_1$ - $C_6$  alkyl;  $C_1$ - $C_4$  haloalkyl;  $C_1$ - $C_4$  alkylthio;  $C_1$ - $C_4$  alkylsulfinyl;  $C_1$ - $C_4$  alkylsulfonyl;  $C_3$ - $C_6$  cycloalkyl optionally substituted with 1-2 methyl groups;  $C_1$ - $C_4$  alkoxy;  $C_1$ - $C_4$  haloalkoxy;  $C_2$ - $C_4$  alkoxyalkyl;  $C_2$ - $C_4$  alkenyl;  $C_2$ - $C_4$  haloalkenyl;  $C_2$ - $C_4$  alkenyloxy;  $C_2$ - $C_4$  alkynyl;  $C_2$ - $C_4$  alkynyloxy;  $NR^{29}R^{30}$ ; or phenyl or phenoxy optionally substituted with  $R^{31}$ ; or

25  $R^9$  and  $R^{13}$ , or  $R^{10}$  and  $R^{13}$ , or  $R^9$  and  $R^{14}$  can be taken together to form  $-(CH_2)_3-$ ,  $-(CH_2)_4-$  or a fused benzene ring optionally substituted with  $R^{31}$ ;

30  $R^{11}$ ,  $R^{12}$ ,  $R^{21}$ ,  $R^{24}$ ,  $R^{26}$  and  $R^{31}$  are each independently halogen;  $C_1$ - $C_4$  alkyl;  $C_1$ - $C_4$  haloalkyl;  $C_1$ - $C_4$  alkoxy; or  $C_1$ - $C_4$  haloalkoxy;

$R^{14}$  is H; halogen;  $C_1$ - $C_2$  alkyl; or  $C_1$ - $C_2$  alkoxy;

35  $R^{15}$ ,  $R^{16}$ ,  $R^{17}$ ,  $R^{18}$ ,  $R^{29}$  and  $R^{30}$  are each independently H or  $C_1$ - $C_2$  alkyl; or

R<sup>15</sup> and R<sup>16</sup>, or R<sup>17</sup> and R<sup>18</sup>, or R<sup>29</sup> and R<sup>30</sup> can be taken together along with the nitrogen atom to which they are attached to form a 4-morpholinyl, pyrrolidinyl or piperidinyl ring;

5 R<sup>20</sup> and R<sup>27</sup> are each independently H; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl; phenylcarbonyl optionally substituted with R<sup>21</sup>; C<sub>3</sub>-C<sub>4</sub> alkenyl; C<sub>3</sub>-C<sub>4</sub> alkynyl; phenylmethyl optionally substituted with R<sup>21</sup> on the phenyl ring; C<sub>1</sub>-C<sub>4</sub> alkylsulfinyl; C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl; phenylsulfinyl, phenylsulfonyl or phenoxycarbonyl each optionally substituted with R<sup>21</sup>; C<sub>2</sub>-C<sub>4</sub> alkoxy carbonyl; C(=O)NR<sup>22</sup>R<sup>23</sup>; C(=S)NHR<sup>23</sup>; 10 P(=S)(C<sub>1</sub>-C<sub>4</sub> alkoxy)<sub>2</sub>; P(=O)(C<sub>1</sub>-C<sub>4</sub> alkoxy)<sub>2</sub>; or S(=O)<sub>2</sub>NR<sup>22</sup>R<sup>23</sup>;

15 R<sup>22</sup> is H or C<sub>1</sub>-C<sub>3</sub> alkyl;

R<sup>23</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl; or phenyl optionally substituted with R<sup>24</sup>; or

20 R<sup>22</sup> and R<sup>23</sup> can be taken together along with the nitrogen atom to which they are attached to form a 4-morpholinyl, pyrrolidinyl, piperidinyl or imidazolyl ring;

25 R<sup>25</sup> is 1-2 halogen; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy; nitro; cyano or C<sub>1</sub>-C<sub>4</sub> alkylthio; and

30 R<sup>28</sup> is halogen; cyano; nitro; hydroxy; hydroxycarbonyl; C<sub>1</sub>-C<sub>6</sub> alkyl; C<sub>3</sub>-C<sub>6</sub> cycloalkyl; C<sub>1</sub>-C<sub>6</sub> haloalkyl; C<sub>1</sub>-C<sub>4</sub> alkylthio; C<sub>1</sub>-C<sub>4</sub> alkylsulfinyl; C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl; (C<sub>1</sub>-C<sub>4</sub> alkyl)<sub>3</sub>silyl; C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl; C<sub>2</sub>-C<sub>4</sub> alkenyl; C<sub>3</sub>-C<sub>4</sub> alkenyloxy; C<sub>2</sub>-C<sub>4</sub> alkynyl; C<sub>3</sub>-C<sub>4</sub> alkynyloxy; C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy; C<sub>2</sub>-C<sub>4</sub> alkoxyalkyl; C<sub>2</sub>-C<sub>5</sub> alkoxy carbonyl; C<sub>2</sub>-C<sub>4</sub> alkoxyalkoxy; NR<sup>15</sup>R<sup>16</sup>; C(=O)NR<sup>17</sup>R<sup>18</sup>; or phenyl,

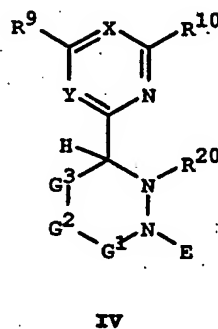
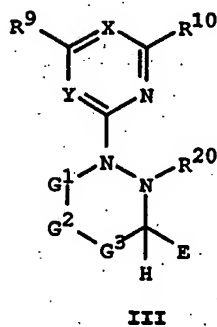
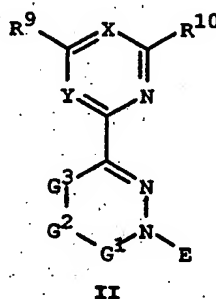
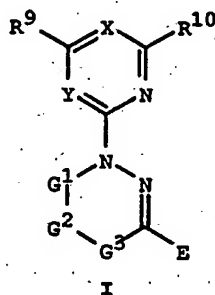


phenoxy or phenylthio each optionally substituted with R<sup>26</sup>.

provided that

when E is, C<sub>1</sub>-C<sub>6</sub> alkylthio, C<sub>1</sub>-C<sub>6</sub> alkoxy, C<sub>1</sub>-C<sub>6</sub> haloalkoxy, phenoxy, phenylthio or phenylamino, then E may only substitute compounds of Formula I.

10. A fungicidal composition comprising a fungicidally effective amount of a compound of Formula I, II, III or IV



15

wherein:

-G<sup>1</sup>-G<sup>2</sup>-G<sup>3</sup>- taken together with the attached atoms form a 5-8 membered ring, wherein

-G<sup>1</sup>- is -CR<sup>1</sup>R<sup>7</sup>-; -(CHR<sup>1</sup>CHR<sup>2</sup>)-; -(CHR<sup>1</sup>CHR<sup>2</sup>CHR<sup>3</sup>)-; or -CHR<sup>1</sup>CHR<sup>2</sup>CHR<sup>3</sup>CHR<sup>4</sup>-;

20

-G<sup>2</sup>- is -O-; -S-; -S(O)-; -S(O)<sub>2</sub>- or -NR<sup>27</sup>-;

$-G^3-$  is  $-CR^4R^8-$ ;  $-(CHR^5CHR^6)-$ ;  $-(CHR^3CHR^5CHR^6)-$  or a direct bond;

X is N or  $CR^{13}$ ;

Y is N or  $CR^{14}$ ;

5 E is H;  $C_1-C_6$  alkyl;  $C_3-C_7$  cycloalkyl optionally substituted with 1-2 methyl;  $C_1-C_6$  haloalkyl;  $C_1-C_6$  alkylthio;  $C_1-C_6$  alkoxy;  $C_1-C_6$  haloalkoxy; or phenyl, phenoxy, phenylthio, phenylamino, phenylmethyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, 2-naphthalenyl, thienyl, furanyl or pyridyl each optionally substituted with  $R^{11}$ ,  $R^{12}$  and  $R^{28}$ ;

10  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are each independently H;  $C_1-C_4$  alkyl;  $C_1-C_4$  haloalkyl, halogen,  $CO_2CH_3$ ,  $CO_2CH_2CH_3$ , cyano or phenyl optionally substituted with  $R^{25}$ ;

15 provided that

- (i) the maximum number of carbon atoms in  $-G^1-G^2-G^3-$  with geminal disubstitution is one;
- 20 (ii) the maximum number of optionally substituted phenyl substituents on  $-G^1-G^2-G^3-$  is one;
- (iii)  $-G^3-$  is other than a direct bond in compounds of Formulae III and IV; and
- 25 (iv)  $-G^2-G^3-$  is other than  $-NR^{27}-$  in compounds of Formulae I and II;

$R^9$ ,  $R^{10}$  and  $R^{13}$  are each independently H; halogen; cyano; hydroxy;  $C_1-C_6$  alkyl;  $C_1-C_4$  haloalkyl;  $C_1-C_4$  alkylthio;  $C_1-C_4$  alkylsulfinyl;  $C_1-C_4$  alkylsulfonyl;  $C_3-C_6$  cycloalkyl optionally substituted with 1-2 methyl groups;  $C_1-C_4$  alkoxy;  $C_1-C_4$  haloalkoxy;  $C_2-C_4$  alkoxyalkyl;  $C_2-C_4$  alkenyl;  $C_2-C_4$  haloalkenyl;  $C_2-C_4$  alkenyloxy;  $C_2-C_4$  alkynyl;  $C_2-C_4$  alkynyloxy;

- NR<sup>29</sup>R<sup>30</sup>; or phenyl or phenoxy optionally substituted with R<sup>31</sup>; or
- 5 R<sup>9</sup> and R<sup>13</sup>, or R<sup>10</sup> and R<sup>13</sup>, or R<sup>9</sup> and R<sup>14</sup> can be taken together to form -(CH<sub>2</sub>)<sub>3</sub>-, -(CH<sub>2</sub>)<sub>4</sub>- or a fused benzene ring optionally substituted with R<sup>31</sup>;
- R<sup>11</sup>, R<sup>12</sup>, R<sup>21</sup>, R<sup>24</sup>, R<sup>26</sup> and R<sup>31</sup> are each independently halogen; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; C<sub>1</sub>-C<sub>4</sub> alkoxy; or C<sub>1</sub>-C<sub>4</sub> haloalkoxy;
- 10 R<sup>14</sup> is H; halogen; C<sub>1</sub>-C<sub>2</sub> alkyl; or C<sub>1</sub>-C<sub>2</sub> alkoxy;
- R<sup>15</sup>, R<sup>16</sup>, R<sup>17</sup>, R<sup>18</sup>, R<sup>29</sup> and R<sup>30</sup> are each independently H or C<sub>1</sub>-C<sub>2</sub> alkyl; or
- R<sup>15</sup> and R<sup>16</sup>, or R<sup>17</sup> and R<sup>18</sup>, or R<sup>29</sup> and R<sup>30</sup> can be taken together along with the nitrogen atom to
- 15 which they are attached to form a 4-morpholinyl, pyrrolidinyl or piperidinyl ring;
- R<sup>20</sup> and R<sup>27</sup> are each independently H; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl; phenyl-carbonyl optionally substituted with R<sup>21</sup>; C<sub>3</sub>-C<sub>4</sub> alkenyl; C<sub>3</sub>-C<sub>4</sub> alkynyl; phenylmethyl optionally substituted with R<sup>21</sup> on the phenyl ring; C<sub>1</sub>-C<sub>4</sub> alkylsulfinyl; C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl; phenylsulfinyl, phenylsulfonyl or phenoxycarbonyl
- 20 each optionally substituted with R<sup>21</sup>; C<sub>2</sub>-C<sub>4</sub> alkoxy carbonyl; C(=O)NR<sup>22</sup>R<sup>23</sup>; C(=S)NHR<sup>23</sup>; P(=S)(C<sub>1</sub>-C<sub>4</sub> alkoxy)<sub>2</sub>; P(=O)(C<sub>1</sub>-C<sub>4</sub> alkoxy)<sub>2</sub>; or S(=O)<sub>2</sub>NR<sup>22</sup>R<sup>23</sup>;
- R<sup>22</sup> is H or C<sub>1</sub>-C<sub>3</sub> alkyl;
- 30 R<sup>23</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl; or phenyl optionally substituted with R<sup>24</sup>; or
- R<sup>22</sup> and R<sup>23</sup> can be taken together along with the nitrogen atom to which they are attached to form a 4-morpholinyl, pyrrolidinyl, piperidinyl
- 35 or imidazolyl ring;

R<sup>25</sup> is 1-2 halogen; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl;  
C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy; nitro; cyano or  
C<sub>1</sub>-C<sub>4</sub> alkylthio; and

5 R<sup>28</sup> is halogen; cyano; nitro; hydroxy; hydroxy-  
carbonyl; C<sub>1</sub>-C<sub>6</sub> alkyl; C<sub>3</sub>-C<sub>6</sub> cycloalkyl; C<sub>1</sub>-C<sub>6</sub>  
haloalkyl; C<sub>1</sub>-C<sub>4</sub> alkylthio; C<sub>1</sub>-C<sub>4</sub> alkyl-  
sulfinyl; C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl; (C<sub>1</sub>-C<sub>4</sub>  
alkyl)<sub>3</sub>silyl; C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl; C<sub>2</sub>-C<sub>4</sub>  
10 alkenyl; C<sub>3</sub>-C<sub>4</sub> alkenyloxy; C<sub>2</sub>-C<sub>4</sub> alkynyl; C<sub>3</sub>-C<sub>4</sub>  
alkynyloxy; C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy;  
C<sub>2</sub>-C<sub>4</sub> alkoxyalkyl; C<sub>2</sub>-C<sub>5</sub> alkoxy carbonyl; C<sub>2</sub>-C<sub>4</sub>  
alkoxyalkoxy; NR<sup>15</sup>R<sup>16</sup>; C(=O)NR<sup>17</sup>R<sup>18</sup>; or phenyl,  
phenoxy or phenylthio each optionally  
substituted with R<sup>26</sup>;

15 provided that

when E is, C<sub>1</sub>-C<sub>6</sub> alkylthio, C<sub>1</sub>-C<sub>6</sub> alkoxy, C<sub>1</sub>-C<sub>6</sub>  
haloalkoxy, phenoxy, phenylthio or phenylamino,  
then E may only substitute compounds of Formula  
I;

20 and agriculturally suitable salts and metal complexes  
thereof and at least one of (a) a surfactant, (b) an  
organic solvent and (c) at least one solid or liquid  
diluent.

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 93/03583

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C07D413/04; C07D417/04; A01N43/88		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C07D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claims No. <sup>13</sup>
P,A	WO,A,9 211 249 (DU PONT DE NEMOURS) 9 July 1992 * claims *	1-10
A	--- CHEMICAL ABSTRACTS, vol. 83, 1975, Columbus, Ohio, US; abstract no. 10171, POTEKHIN, A. A., NIKOLAEVA, N. M. '5,6-Dihydro-4H-1,3,4-oxadiazines.' see abstract & SU,A,461 929 28 February 1975 cited in the application --- -/--	1-10
<p>* Special categories of cited documents : <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search 13 JULY 1993		Date of Mailing of this International Search Report 26. 07. 93
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer Bernd Kissler

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category <sup>a</sup>	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	CHEMICAL ABSTRACTS, vol. 90, 1979, Columbus, Ohio, US; abstract no. 152131, DOVLATYAN V V; GEVORKYAN R A 'Synthesis of pesticides. Reactions of halonitriles with esters of s-triazinyldithiocarbazic acid.' see abstract & ARM. KHIM. ZH. (AYKZAN,05159628); 78; VOL.31 (11); PP.851-6	1-10
A	CHEMICAL ABSTRACTS, vol. 87, 1977, Columbus, Ohio, US; abstract no. 102359, DOVLATYAN V V; GEVORKYAN R A 'Synthesis of pesticides. II. Study of the reaction of potassium hydrazino-s-triazine with chloroacetonitrile and .alpha.,.beta.-dichloropropionitrile and its urotropine salt' see abstract & ARM. KHIM. ZH. (AYKZAN,05159628); 77; VOL.30 (10); PP.851-4	1-10
A	CHEMICAL ABSTRACTS, vol. 89, 1978, Columbus, Ohio, US; abstract no. 43349, DOVLATYAN V V; GEVORKYAN R A 'Oxadiazinyl-s-triazine derivatives' see abstract & SU,A,556 143 (ARMENIAN AGRICULTURAL INSTITUTE; USSR) 30 April 1977	1-10

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 93/03583

## Box I Observations where certain claims were found unsearchable. (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/

The definition of the following substituent(s) is too general and/or encompasses too broad a range of totally different chemical groups, only partly supported by examples given in the descriptive part of the application:

X, Y, G1, G2, G3, E

The number of theoretically conceivable compounds resulting from the combination of all claimed substituents of above list precludes a comprehensive search. Guided by the spirit of the application and the inventive concept as disclosed in the descriptive part of the present application the search has been limited to the following case(s):

1. 4-(2-Pyridyl or 2-Pyrimidyl or 2-Triazinyl)-1,3,4-Oxa/thiadiazines
2. 4-(2-Pyridyl or 2-Pyrimidyl or 2-Triazinyl)-1,3,4-Oxa/thiadiazepines
3. 4-(2-Pyridyl or 2-Pyrimidyl or 2-Triazinyl)-1,3,4-Oxa/thiadiazocines



US 9303583  
SA 73324

**13/07/93**

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9211249	09-07-92	AU-A- 9127091 CN-A- 1062726	22-07-92 15-07-92

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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